Supporting Information for

**Ion-Molecule Complex Dissociation and Formation Dynamics in LiCl Aqueous Solutions
from 2D IR Spectroscopy**

Rongfeng Yuan, Chang Yan, and Michael Fayer*
Department of Chemistry
Stanford University, Stanford, CA 94305
*phone: 650 723-4446; email: fayer@stanford.edu

1. Frequency-Frequency Correlation Function (FFCF)

The FFCF is the probability that a vibration with an initial frequency in the inhomogeneous
spectral distribution still has the same frequency at a later time, averaged over all initial
frequencies. The FFCF is quantified via a 2D line shape analysis known as the center line slope
(CLS) method. A fit to the CLS vs T_w curve, which is the normalized FFCF, gives spectral
diffusion time constants and amplitude factors. The FFCF can be modeled as a sum of
exponential:

$$C(t) = \langle \delta\omega(t)\delta\omega(0) \rangle = \sum_i \Delta_i^2 \exp(-t/\tau_i) \tag{S1}$$

Here, $\delta\omega(t) = \omega(t) - \langle \omega \rangle$ is the instantaneous frequency fluctuation with $\langle \omega \rangle$ being the average
frequency. Δ_i is the frequency fluctuation amplitude of each component, and τ_i is its associated
time constant. A component of the FFCF with $\Delta_i\tau_i < 1$ is motionally narrowed. When a
component is motionally narrowed, Δ and τ cannot be determined separately. The motionally
narrowed homogeneous contribution to the absorption spectrum has a pure dephasing linewidth
given by $\Gamma^* = \Delta^2\tau = 1/\pi T_2^*$, where T_2^* is the pure dephasing time. The observed homogeneous
dephasing time, T_2, also has contributions from the vibrational lifetime and reorientational
relaxation:

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2T_1} + \frac{1}{3T_{or}} \tag{S2}$$

where T_2^*, T_1, and T_{or} are the pure dephasing time, vibrational lifetime, and orientational
relaxation times, respectively. The total homogeneous line width is $\Gamma = 1/\pi T_2$. The total
homogeneous dephasing time T_2 and the values of Δ_i in units of frequency are obtained from the

experimental data by a simultaneous fit to the CLS decay and the experimental linear absorption line shape. Usually, T_1 and T_{or} are sufficiently slow compared to T_2^* that $T_2^* \approx T_2$. It is important to note that the CLS decay is an experimental observable that is independent of a specific dynamic model. The exponential time constants characterize the time scale of the observed dynamics rather than being strictly associated with a single structural event.

2. Determination of transition dipole ratio

The diagonal peak volumes V_W and V_L are proportional to the fourth power of the corresponding transition dipole moment, i.e., $V_W(t) \propto N_W(t)\mu_W^4$, and $V_L(t) \propto N_L(t)\mu_L^4$. The two off-diagonal peak volumes V_{WL} and V_{LW} are both proportional to $\mu_W^2\mu_L^2$. It is necessary to know the ratio of the two transition dipoles, not their absolute values. The ratio is determined in the following manner. At very early T_w (<1.5 ps) when exchange is not significant, the peak volumes are proportional to the equilibrium concentrations. Thus,

$V_W(t \approx 0) \propto N_W(t=0)\mu_W^4$ and $V_L(t \approx 0) \propto N_L(t=0)\mu_L^4$. In the linear IR absorption spectrum, the peak areas, S_i, are proportional to the product of the equilibrium concentrations and the transition dipoles squared, i.e., $S_W \propto N_W(t=0)\mu_W^2$ and $S_L \propto N_L(t=0)\mu_L^2$. The two peak areas were obtained from the Voight fitting shown in Fig. 4A. The combination of these data yields the ratios $N_W(t=0)/N_L(t=0)$ and μ_W^2/μ_L^2, and the latter ratio is 0.70 ± 0.07 for all 3 LiCl concentrations. These two ratios directly fix the ratio between k_{WL} and k_{LW}, reducing by one dimension the fitting function. μ_W/μ_L was used to obtain the populations from the peak volumes.

3. Heating Background Subtraction method

Intense IR pulses can cause temperature increases in the sample. Some molecule's infrared absorption spectra can be shifted due to temperature rising. Therefore, heating signal arises from the IR absorption spectra difference between pump pulses "on" and "off", and this signal interferes with the analysis of resonance signal. It usually grows with the vibrational relaxation lifetime as the excited states dump energy into the bath environment, increasing the overall temperature of the surrounding.[1,2]

Water and aqueous solutions have significant IR absorption in a wide range of infrared frequencies, which can produce time dependent heating signals. This was observed very early when HOD was used as a vibrational probe to examine hydrogen bond dynamics. In the sample investigated here, there is heating signal not only from water but also from the probe molecule MeSCN. These two heating signals have different spectral features and therefore have to be treated differently. Because of the broad IR absorption of water, there is a heating signal in the observed IR frequency range 2110 cm^{-1} to 2210 cm^{-1} that grows in as an increasing positive offset across the entire MeSCN spectrum. There are additional very weak but highly structured signals that can be observed at the long time end of the chemical exchange measurements. These signals have positive and negative going features, some of which overlap the MeSCN 2D spectra. These structured heating peaks are so weak that they cannot be observed at the earlier T_ws because of the strong resonant signals but are not insignificant at the longer T_ws.

To obtain the time dependence of the growth of the broad signal, PPSP experiments were first conducted on a background sample without MeSCN to measure the rate of increase of the heating signals. The example of LiCl 1:5 H_2O solution is presented in Fig. S1 A. The growth of heating signal was fit with a biexponential function with time constants 0.8 ps and 3.2 ps. These values barely changed across the LiCl concentration range. Then, real samples and background samples were measured at the same series of waiting times, T_w, as used in the vibrational echo experiments. At $T_w = 500$ ps when no resonance signal is left and heating signal is constant, signal of background sample were scale-subtracted from the real sample so that the region of the higher ω_m frequencies 2190 cm^{-1} to 2220 cm^{-1} had no signal. Then 2D spectra at other T_ws were processed using the same scaling factor. Next, to remove the more structured heating features, they were observed at very long T_w, usually 500 ps. 500 ps is longer than 10 times the CN stretch lifetime, so the resonant signal has decayed to zero, and the heating signal is constant. It was assumed that the very weak structured heating features grow in at the same rate as the broad feature. An exponential growth model of 2D spectra heating background, with time constants from the PSPP measurement and final amplitudes from the long T_w 2D measurements was used to subtract the heat induced signals. The two panels of Figure S1 B show the magnitude of heating signal compared to the overall signal obtained at 17 ps. The heating signal is relatively

small. The procedure is robust because a small error in subtraction of a small signal does not affect the results presented in the main text. Tests were made in which the time constants for the growth of the structured heating signals were varied over a wide range with no significant effect within experimental error on the data analysis presented in the main text.
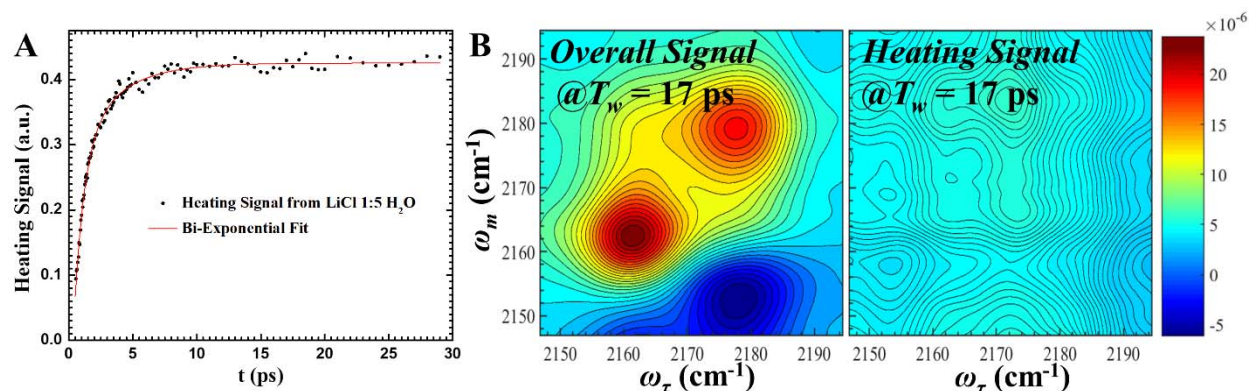

Figure S1. A represents the growth of heating signal measured by PSPP in the background sample LiCl 1:5 H_2O solution without the probe MeSCN. The red line is the biexponential fit to the data. The two panels of **B** show the magnitude comparison between the overall signal and heating signal in isotropic polarization setting at 17 ps in LiCl 1:5 H_2O solution. The first panel is the 2D spectrum obtained directly from experiments, including both resonance and heating signals. The heating signal spectrum includes contribution from both water and the probe. The two spectra share the same color map that is shown on the right.

References

1. Steinel, T.; Asbury, J. B.; Zheng, J. R.; Fayer, M. D., Watching hydrogen bonds break: A transient absorption study of water. *J. Phys. Chem. A* **2004,** *108* (50), 10957-10964;

2. Giammanco, C. H.; Wong, D. B.; Fayer, M. D., Water Dynamics in Divalent and Monovalent Concentrated Salt Solutions. *J. Phys. Chem. B* **2012,** *116*, 13781-13792.