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Vibrational Energy Transfer: An Angstrom Molecular Ruler

- in Studies of Ion Pairing and Clustering in Aqueous Solutions

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ABSTRACT

The methodology and principle using vibrational energy transfer to measure molecular distances in liquids are introduced. The application of the method to the studies of ion pairing and clustering in strong electrolyte aqueous solutions is demonstrated with MSCN aqueous solutions where M = Li, Na, K, Cs, and NH₄. Experiments suggest that ions in the concentrated aqueous solutions can form substantial quantities of ion clusters in which both cations and anions are involved. More and larger clusters form in solutions that are relatively more concentrated and which include a larger cation. In KSCN solutions, the shortest anionic distance in the ion clusters is the same as that in the KSCN crystal. The rotational time of the anion and the nonresonant vibrational energy transfer time with a gap of 75 cm⁻¹ in the KSCN saturated solution are very

1
2
3 similar to those in the KSCN crystal. However, the KSCN ion clusters are closer in structure to
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5 the melt. The clusters form an interconnected network with random ionic orientations. Because
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7 of ion clustering, the anion and water dynamics behave distinctly in the same solutions. At high
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9 concentrations, the anion rotation significantly slows down because of the increase in the size of
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11 the ion clusters, but the slowdown amplitude of water rotation is very modest because many of
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13 the water molecules still remain in the “bulk” state due to ion clustering. The rotational dynamics
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15 of both water and anions are slower in a solution with a smaller cation, primarily because a
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17 smaller cation has a stronger cation/anion interaction and a cation/water interaction that leads to
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19 more water molecules confined in the ion clusters. Adding ions or molecules into the KSCN
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21 solutions can perturb the ion clusters. Weakly hydrated anions can participate in clustering and
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23 form mixed ion clusters with KSCN, and strongly hydrated anions can reduce the effective water
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25 molecules solvating KSCN and facilitate the formation of more and larger KSCN ion clusters.
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27 Similarly, molecules which can strongly bind to SCN^- prefer to participate in the KSCN ion
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29 clusters. Molecules which are strongly hydrated prefer to remain hydrated and facilitate the ion
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31 clustering of KSCN.
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1. Introduction

In nature, electrolyte aqueous solutions are ubiquitous and essential for many chemical processes and life phenomena. In solutions, reaction kinetics and selectivity as well as biological functions are closely correlated to, and in some cases even determined by the dynamics and structures of the solutions.¹ The research on water and its solutions has a very extensive history.²⁻¹⁵ It has long been known that the properties of strong electrolyte aqueous solutions deviate from those of ideal solutions already at exceedingly low concentrations ($<10^{-5}$ M). The deviations were proposed to be caused by the attraction and repulsion of ions, leading to the development of the Debye-Hückel theory.^{15,16} However, at slightly higher concentrations ($\sim 10^{-3}$ M), even this theory fails and the formation of ion pairs containing ions of opposite charge has been believed to be mainly responsible for this failure.^{2,3} Previous molecular dynamics (MD) simulations, suggested that clusters with more than two ions can exist, and these clusters could be a major factor causing the non-ideality of the solutions at medium and high concentrations.¹⁶⁻¹⁹

For unsaturated solutions of complex salts with ions of multiple charges, the presence of large ion clusters has been experimentally demonstrated, albeit with a number of assumptions in the interpretation of measurements.²⁰⁻²² For solutions with simple ions of mono charge (illustrated in fig.1A), MD simulations predict the presence of small clusters containing only a few ions. The detection of these small clusters with the usual tools for probing structures in liquids, e.g. neutron or X-ray diffraction,²³ or dynamic light scattering,^{18,24} is extremely challenging, because compared to the contributions from water-water and water-ion interactions the contribution of ion-ion correlations to the total scattering pattern is small.¹⁸ It is also very difficult to identify these ion clusters by the routine FTIR, Raman or NMR measurements, because in general there are not quantitative correlations between the vibrational frequencies or

chemical shifts of the ions and the ionic distances (fig.11 in section 4.8 is one example).²⁵ Furthermore, the frequency shifts caused by clustering can be small relative to the peak widths.²⁶ Electronic energy transfer methods, e.g. FRET,^{27,28} are not suitable to measure these ion clusters either, because they typically require the labels of large chromophores (>1~2nm) which are much larger than simple ions and can significantly perturb the ionic interactions.

Very recently, we found that ion pairing and clustering in aqueous solutions of mono-charged ions can be directly observed with the vibrational energy transfer method using ultrafast vibrational spectroscopy.^{26,29-35} The vibrational energy transfer method involves the measurement of the rate of energy transfer between two vibrational modes located on two ions.^{29,34} The energy transfer relies on the dipole-dipole coupling of the two modes and thus depends strongly on the distance between the ions. Hence, the energy transfer rate can be converted to the distance between two ions.^{32,33} In aqueous solutions, the distance between two ions is typically larger than the length of a chemical bond (or a vibrational mode), and the vibrational coupling between two modes is typically smaller than the vibrational dephasing line widths of the modes.^{32,33} As a result, the energy transfer can be described in the weak coupling limit using point dipoles, leading to an energy transfer rate constant k that strongly decreases with increasing distance r , approximately following $k \propto r^{-6}$.^{32,33} In general, water-solvated ions and water solvent-separated ion pairs have much larger inter-ionic distances than contact ion pairs. Therefore, the vibrational energy transfer method primarily probes the contact ion pairs.

In this work, we will introduce the principle of the vibrational energy transfer method, the experimental setup and procedure to quantitatively obtain the vibrational energy transfer rate constant and to convert the rate constant into the ionic distance, and the application of the method to the studies of ion pairing and clustering in strong electrolyte aqueous solutions.

2. Theoretical Background of Intermolecular Vibrational Energy Transfer

Energy transfer from one level of one molecule to another level of another molecule in a condensed phase is one of the most fundamental molecular phenomena. It has been studied for many years in the energy ranges of both electronic and vibrational excitations.^{27,36-41} Intermolecular energy transfers can go through the coherent process if the donor/acceptor coupling is so strong that it is comparable to or even larger than the dephasing line width of the donor/acceptor coherence ($V_{DA} \geq \tau^{-1}$, both defined in eq.1),^{32,42,43} or go through the hopping process if the coupling is weak.^{32,42} For most intermolecular vibrational energy transfers in a condensed phase, they follow the hopping process, because the donor/acceptor coupling strength, which can be simply estimated based on eq.2 with the transition dipole moment 0.2~0.4D and the donor/acceptor distance 0.3~1 nm, is usually a few cm^{-1} or smaller, smaller than the typical line width ($>10 \text{ cm}^{-1}$) of a vibrational mode which is at the same order of magnitude of the donor/acceptor coherence dephasing line width.^{32,33}

In a condensed phase, the energy of a molecular vibration is a distribution (a peak) rather than a single value (a line) because of molecular motions and interactions. Traditionally, an energy transfer of which the donor and acceptor have the same central energy value is called resonant energy transfer. An energy transfer with donors/acceptors of different central energy values is called nonresonant energy transfer. For the hopping process, the resonant energy transfer follows the **dephasing** mechanism.^{32,33} The mechanism can be described as following: In an energy transfer system, because the energy donor state and the energy acceptor state are coupled, according to quantum mechanics, the two states form a coherence. Without any external perturbation, the excitation (or energy) will oscillate back and forth between the donor state and the acceptor state in a coherent manner. In a condensed phase at temperatures higher than 0 K,

molecules are constantly moving. Such thermal motions inevitably cause some random molecular collisions against either the donor or acceptor or both. The collisions can shift the molecular frequencies suddenly and cause the coherence between the donor and the acceptor to dephase. Because of the dephasing, the excitation (or energy) has a certain probability at the acceptor state and doesn't go back to the donor state, resulting in the completion of one energy transfer.^{32,33} Integrating all dephasing events, the energy transfer rate can be quantitatively described by the following equation^{32,33}

$$k_{DA} = \frac{2}{1 + e^{-\frac{\Delta\omega_{DA}}{RT}}} V_{DA}^2 \frac{\tau^{-1}}{(\Delta\omega_{DA})^2 + 4V_{DA}^2 + \tau^{-2}}, \quad (1)$$

where $\Delta\omega_{DA} = \omega_D - \omega_A$, the difference between the central energy values of D and A, also termed the donor/acceptor (D/A) energy gap (this value is equal to 0 for the resonant energy transfer). τ is the dephasing time of the coherence between the donor and acceptor. V_{DA} is the D/A coupling strength³² which is related to the D/A distance (r_{DA}) under the transition-dipole/transition-dipole interaction mechanism by²⁸

$$V_{DA}^2 = \frac{1}{n^4} \frac{\mu_D^2 \mu_A^2}{(4\pi\epsilon_0)^2} \frac{\kappa^2}{r_{DA}^6}, \quad (2)$$

where n is the refractive index. μ_D and μ_A are the respective transition dipole moments of the donor and acceptor. ϵ_0 is the vacuum permittivity. r_{DA} is the distance between the donor and acceptor. κ is the orientation factor dependent on the relative orientations of the donor/acceptor and the relative time scales of the rotations of the donor/acceptor and the energy transfer.³³ For simple ions in room temperature aqueous solutions, the rotations of ions are much faster than the vibrational energy transfer between two ions, and therefore κ equals $\sqrt{2/3}$ which is the average value over all angles.^{29,32} The combination of eqs. 1&2 to convert the energy transfer rate

constant k_{DA} into the D/A distance r_{DA} has been experimentally benchmarked with the KSCN isotope mixed crystals.³³ In the crystals, the distance between any two thiocyanate anions is well defined and characterized with XRD and the vibrational energy transfer rate constant between them is determined by the vibrational energy transfer method.³³ The distance determined by the vibrational energy transfer method is the same as that determined by XRD.³³

Unlike the resonant energy transfer, two mechanisms play roles simultaneously in nonresonant vibrational energy transfer:^{32,33} (1) the dephasing mechanism (eq.1) which is exactly the same as that for the resonant energy transfer; and (2) the phonon compensation mechanism.⁴⁴⁻⁴⁷ This is because in a nonresonant energy transfer system, there is always a certain chance that the energy distributions of the donor and acceptor molecules can overlap. As a result, the energy can transfer between the donor and acceptor resonantly through the overlapped portion (the dephasing mechanism). At the same time, energy of any donor molecule can always transfer to an acceptor molecule with a different energy value if the D/A energy gap can be compensated by the phonons in the system (the phonon compensation mechanism). Dependent on the details of a particular situation, one mechanism can be dominant over the other. For instance, examining the nonresonant vibrational energy transfers among the nitrile stretches in the KSCN isotope mixed crystals, the phonon compensation mechanism is dominant, while in the liquid solutions of these mixed crystals the dephasing mechanism plays a larger role.^{32,48} Our recent energy gap dependent energy transfer experiments and theoretical derivations⁴⁸ suggest that, at room temperature, the contribution from the phonon compensation is much smaller than that from the dephasing mechanism for most nonresonant intermolecular vibrational energy transfers in liquids with energy gaps smaller than the thermal energy ($\Delta\omega_{DA} < RT \sim 200 \text{ cm}^{-1}$). In other words, these nonresonant energy transfers can be quantitatively described by eq.1. The

phonon compensation mechanism is not significant in liquids because of the very fast molecular motions. In liquids, molecular motions (e.g. rotations and translations of a few angstroms) are much faster than the energy transfer process. Therefore, before the energy transfer occurs, the fast molecular motions can cause the positions or phases of the donor and acceptor relative to the phonons to fluctuate or even exchange. This significantly reduces the difference between the phonon modulations on the donor and the acceptor, causing the efficiency of phonon compensation for the D/A gap to diminish.⁴⁸ Nonresonant energy transfers with larger gaps ($>200\text{ cm}^{-1}$) are typically very slow ($\sim \geq 1\text{ ns}$), at times two or three order magnitudes slower than intramolecular vibrational relaxations. Experimentally it is very challenging to detect such slow energy transfers because of the extremely low signal levels.

As discussed above, for most cases in liquids, both resonant and nonresonant vibrational energy transfers can be described by eq.1. In eq.1, there are two unknown parameters: the coupling strength V_{DA} and the dephasing line width τ^{-1} . To quantitatively determine both parameters, the energy transfer rate constants (k_{DA}) for at least two energy gaps ($\Delta\omega_{DA}$) must be determined. The gap dependent measurements can be experimentally achieved by isotope labeling of the donor or acceptor to shift their vibrational frequencies. This is considered a perturbation-free label method, as the isotope substitution does not change the electronic structure or intermolecular interactions.^{30,32,48} Once V_{DA} is determined from the experiments, the D/A distance r_{DA} can be obtained by plugging V_{DA} into eq.2. For some systems, isotope labels may not be immediately available and only one energy transfer rate constant for one energy gap is available. In this situation, to obtain V_{DA} , we need to estimate the dephasing line width τ^{-1} . According to the derivation of eq.1, the D/A coherence dephasing line width τ^{-1} must not be

larger than the sum ($\tau_D^{-1} + \tau_A^{-1}$) of the donor and acceptor line widths, $\tau^{-1} \leq \tau_D^{-1} + \tau_A^{-1}$.³² If D/A dephasings are correlated, $\tau^{-1} < \tau_D^{-1} + \tau_A^{-1}$. If they are uncorrelated, $\tau^{-1} = \tau_D^{-1} + \tau_A^{-1}$. All of our previous experiments on energy transfers among the nitrile stretches in thiocyanate solutions show that the donor and acceptor dephasings are correlated. The D/A coherence dephasing line width τ^{-1} is only 50%~80% of the sum ($\tau_D^{-1} + \tau_A^{-1}$) of the donor and acceptor line widths. We suspect that this is because the D/A distances in these systems are only about 0.4 nm which are so short that the dephasing of the donor inevitably affects that of the acceptor, and vice versa. Only at much larger distances where D/A dephasings are uncorrelated, the D/A coherence dephasing line width is equal to the sum of the donor and acceptor line widths, $\tau^{-1} = \tau_D^{-1} + \tau_A^{-1}$. Under this condition, eq.1 becomes the Förster energy transfer equation - the energy transfer rate is determined by the D/A spectral overlap.³² Therefore, based on our previous experimental results, using 50% of the D/A homogenous line width sum for the D/A coherence dephasing line width τ^{-1} for vibrational energy transfers with D/A distances smaller than 1nm is probably a reasonable starting point to estimate V_{DA} from a measured value of k_{DA} .

3. Experimental Section

Vibrational energy transfer kinetics were measured in real time using the ultrafast multiple-mode multiple-dimensional vibrational spectroscopy. The details of the technique were described previously.^{49,50} Briefly, a ps amplifier (~1 ps) and a fs (~38 fs) amplifier are synchronized with the same seed pulse from a 76 MHz oscillator. The output of the ps amplifier pumps an OPA to produce ~0.8 ps IR pulses with a bandwidth of 10~35 cm^{-1} in a tunable range from 500 cm^{-1} to 4000 cm^{-1} with energy 1~40 μJ /pulse at 1 KHz. Light from the fs amplifier is directed to generate a <100 fs ultra-broadband mid-IR and terahertz super-continuum pulse in the

frequency range from $<10\text{ cm}^{-1}$ to $>3500\text{ cm}^{-1}$ at 1 KHz.^{50,51} In nonlinear IR experiments, the ps IR pulse is the excitation beam of which the excitation power is adjusted based on need. The interaction spot varies from 100 to 500 microns. The super-continuum pulse is the detection beam. Its frequency is resolved by a spectrograph with a resolution of $1\sim3\text{ cm}^{-1}$ which is dependent on the central frequency, yielding the detection axis of a 2D IR spectrum. Two polarizers are inserted into the detection path to selectively detect the parallel or perpendicular polarized signal relative to the excitation beam. Excitation populations in nonresonant energy transfer experiments and vibrational lifetimes are obtained from the rotation-free 0-1 (between the ground state and the 1st vibrational excited state) or 1-2 (between the 1st excited state and the 2nd excited state) transition signal $P_{life} = P_{\parallel} + 2 \times P_{\perp}$, where $P_{\parallel}$, $P_{\perp}$ are parallel and perpendicular data respectively. The reorientational motions and resonant energy transfers are monitored by acquiring the waiting time dependent anisotropy values $r(t) = (P_{\parallel} - P_{\perp}) / (P_{\parallel} + 2 \times P_{\perp})$. This is because the anisotropy values usually decay with waiting time t as a result of two possible molecular origins: the molecular reorientation and resonant energy transfers to molecules in different orientations. Both dynamics contribute to the orientational randomization of vibrational excitations and result in the decay of signal anisotropy.⁴⁹ For all experiments, the signal resulting from vibrational relaxation induced heat is removed with the procedure described previously.^{29,52-54} Viscosities of the samples were measured at room temperature with a Cannon–Fenske kinematic viscosity tube.

4. Results and Discussions

4.1 Nonresonant Vibrational Energy Exchange between Thiocyanate Anions

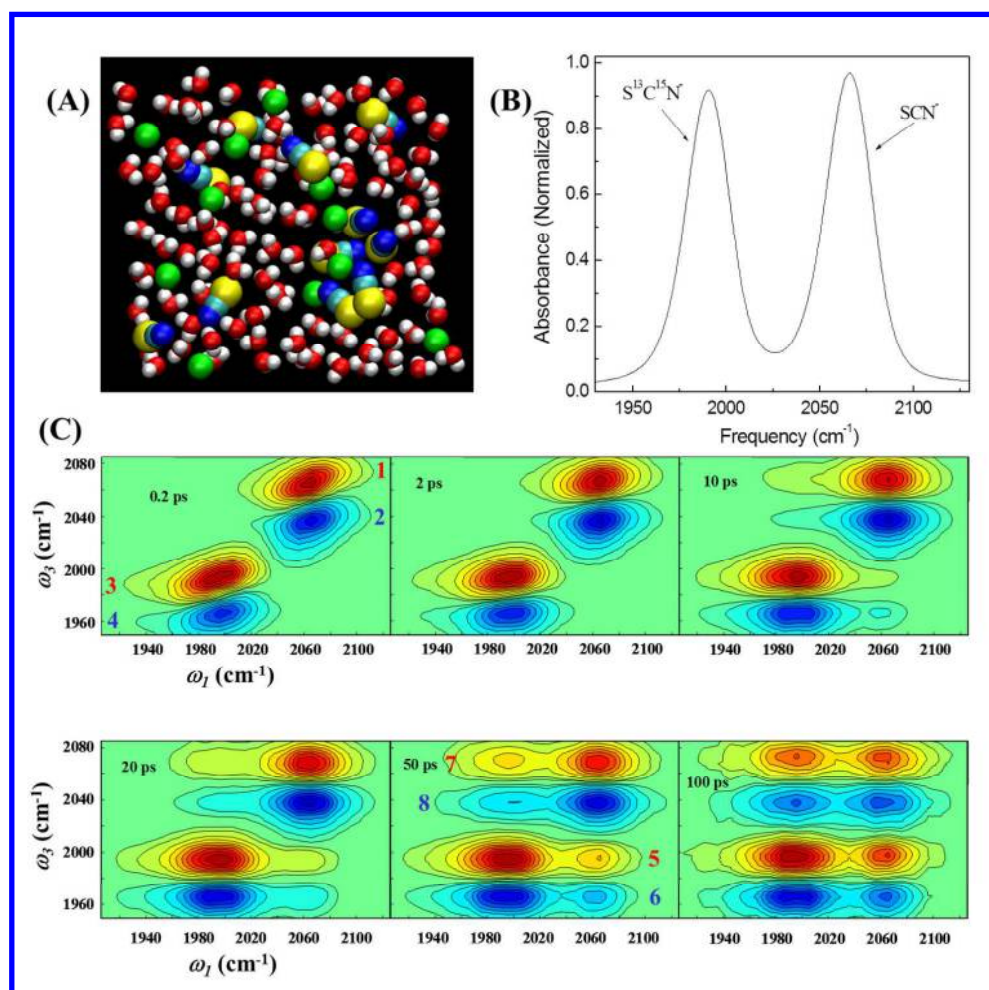
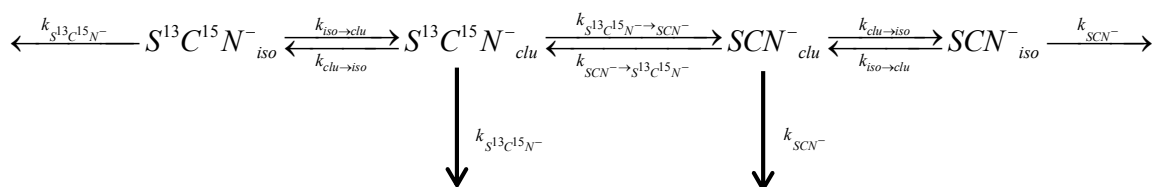


Figure 1. (A) A snapshot of a 1.8M KSCN aqueous solution obtained from MD simulation, with O (red), H (white), C (light blue), N (deep blue), K (green) and S (yellow). Some water molecules are removed to better display the cluster structure. (B) FTIR spectrum of the CN and $^{13}C^{15}N$ stretches of SCN^- and $S^{13}C^{15}N^-$ of a 10M KSCN/ $KS^{13}C^{15}N \sim 1/1$ aqueous solution. (C) The waiting time dependent 2D IR spectra of the 10M solution. As T_w increases, the off-diagonal peaks appear due to vibrational energy exchange between SCN^- and $S^{13}C^{15}N^-$.²⁹ Reprinted with permission from Reference 29 (Bian, H.; Wen, X.; Li, J.; Chen, H.; Han, S.; Sun, X.; Song, J.; Zhuang, W.; Zheng, J. Ion Clustering in Aqueous Solutions Probed with Vibrational Energy Transfer. *Proc. Nat. Acad. Sci.* **2011**, 108, 4737-4742).

The nonresonant vibrational energy transfer between two ions is measured with the vibrational energy exchange method.^{29,52,53} Here we use a saturated (10 M) KSCN/KS¹³C¹⁵N ~ 1/1 D₂O solution at room temperature to demonstrate how to quantitatively obtain the vibrational energy transfer rate constant.²⁹ Fig.1B shows the FTIR spectrum of the CN and ¹³C¹⁵N⁻ stretches of SCN⁻ and S¹³C¹⁵N⁻ in the solution.²⁹ The isotope labeling shifts the CN stretch 0-1 transition frequency from 2066 cm⁻¹ (SCN⁻) down to 1991 cm⁻¹ (S¹³C¹⁵N⁻). In Fig.1C the time evolution of 2D-IR vibrational spectrum of these modes is presented. The two diagonal peak pairs 1~4 represent the anions that have not transferred their energy. At a very short waiting time T_w (200 fs), when a negligible amount of vibrational energy exchange has occurred, the spectrum contains only diagonal peak pairs. Peaks 1 & 2 represent the 0-1 and 1-2 transitions of the CN vibration of SCN⁻. Peaks 3 & 4 correspond to the 0-1 and 1-2 transitions of the ¹³C¹⁵N⁻ vibration of S¹³C¹⁵N⁻. With the increase of T_w , an increasing amount of vibrational energy has been transferred between the two anions. Cross peak pairs 5~8 begin to appear in the off-diagonal position. These new peaks arise from the transfer of vibrational energy. The energy transfer from SCN⁻ to S¹³C¹⁵N⁻ produces Peaks 5 & 6. These peaks are located at the excitation frequency $\omega_1 = 2066\text{ cm}^{-1}$, corresponding to the 0-1 transition frequency of the CN stretch of SCN⁻, and the detection frequencies $\omega_3 = 1991\text{ cm}^{-1}$ and 1966 cm^{-1} that correspond to the 0-1 and 1-2 transition frequencies of the ¹³C¹⁵N⁻ stretch vibration of S¹³C¹⁵N⁻, respectively. Likewise, Peaks 7 & 8 are produced by energy transfer from S¹³C¹⁵N⁻ to SCN⁻. At each waiting time, Peaks 5&6 are larger than Peaks 7&8. The trend can be more clearly seen in Fig.2B. This is because of the detailed principle which states that the energy transfer from one level to a lower one is faster than the reverse process. The rate ratio of these two processes is the Boltzmann factor determined by the energy gap ($k_{DA} / k_{AD} = \exp[(\omega_D - \omega_A) / RT]$).

To quantitatively analyze the energy transfer kinetics from the 2D IR measurements in Fig.1C, we constructed a kinetic model. The solution is saturated, and therefore some ions inevitably form clusters, as required by chemical equilibrium. The anions in the clusters are close to each other and hence can transfer energy efficiently. Other anions in the saturated solution solvated by water molecules are well separated and less able to transfer energy. Both clustered and solvated anions are not frequency resolvable, and produce diagonal peak pairs together in the 2D IR spectra in Fig.1C. However, the cross peak pairs mainly originate from the clustered anion since the clustered anions can exchange energy with a much higher efficiency due to the shorter anionic distances in the clusters. Simultaneous analyses of diagonal and cross peaks provide not only the energy exchange rate constants, but also the ratio of clustered to separated anions. Based on the physical picture, a location-energy-exchange kinetic model has been developed.^{29,49} Briefly, in the solution, some anions $S^{13}C^{15}N^-$ and SCN^- form clusters (denoted as $S^{13}C^{15}N^-_{clu}$ and SCN^-_{clu}), and the rest anions are separated by water (denoted as $S^{13}C^{15}N^-_{iso}$ and SCN^-_{iso}). Both anions are in dynamic equilibrium. They can exchange locations with rate constants $k_{clu \rightarrow iso}$ and $k_{iso \rightarrow clu}$. The equilibrium constant $K = k_{iso \rightarrow clu} / k_{clu \rightarrow iso}$ is determined by the principle of microreversibility. The clustered anions $S^{13}C^{15}N^-_{clu}$ and SCN^-_{clu} can exchange vibrational energy with the rate constants $k_{S^{13}C^{15}N^- \rightarrow SCN^-}$ and $k_{SCN^- \rightarrow S^{13}C^{15}N^-}$. The ratio $D = k_{S^{13}C^{15}N^- \rightarrow SCN^-} / k_{SCN^- \rightarrow S^{13}C^{15}N^-}$ is determined by the detailed balance principle. The energy transfer rate for the separated anions is assumed to be negligibly small because of the relatively long distance between them. In other words, the isolated anions cannot transfer vibrational energy with other isolated anions or with the clustered anions. The vibrational excitations of $S^{13}C^{15}N^-$ and SCN^- decay with each species having its own vibrational relaxation rate constant

$k_{S^{13}C^{15}N^-}$ and k_{SCN^-} . We simply assume that for each CN stretch, the vibrational lifetimes of clustered and isolated species are the same, because experimentally these two species are not resolvable. By using rotation-free data ($P_{life} = P_{||} + 2 \times P_{\perp}$) the model does not contain any rotational component. The model is described in the following scheme



(Scheme 1. Location-energy-exchange kinetic model)

Based on the kinetic model in Scheme 1, four differential equations are derived.²⁹ There are only three unknown parameters to be determined because the vibrational relaxation rate constants can be experimentally determined, the ratio of the location exchange rate constants ($k_{clu \rightarrow iso}$ and $k_{iso \rightarrow clu}$) is the equilibrium constant, and the ratio of the energy transfer rate constants is determined by the detailed balance. By solving the equations, the energy transfer rate constants, the clustered/separated ion equilibrium constant and the location exchange rate constants are obtained. Simultaneous analyses of the time dependent intensities of peaks 1, 3, 5&7 according to the vibrational energy exchange kinetic model show that the energy transfer time ($1/k_{SCN^- \rightarrow S^{13}C^{15}N^-}$) from SCN^- to $S^{13}C^{15}N^-$ is 115 ± 15 ps, the equilibrium constant $K = 19 \pm 3$, and the location exchange rate constants $1/k_{clu \rightarrow iso} = 12 \pm 7$ ps. Detailed parameters of the calculations can be found in the supporting materials of our previous publication.²⁹ Calculations simultaneously well fit the four experimental curves, as shown in Fig. 2A and 2B. The equilibrium constant $K = 19 \pm 3$ indicates that more than 95% of anions form clusters in KSCN saturated aqueous solution. The ion cluster ratio is surprisingly large.

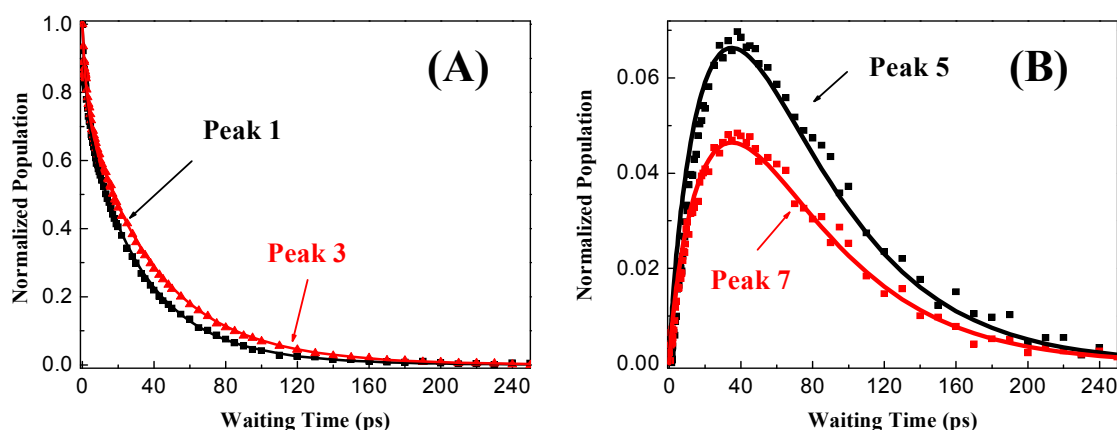


Figure 2. The waiting time dependent intensities of peaks 1, 3, 5, 7 in Fig.1C. Dots are experimental data, and curves are calculated results based on the kinetic model.²⁹ Adapted with permission from Reference 29 (Bian, H.; Wen, X.; Li, J.; Chen, H.; Han, S.; Sun, X.; Song, J.; Zhuang, W.; Zheng, J. Ion Clustering in Aqueous Solutions Probed with Vibrational Energy Transfer. *Proc. Nat. Acad. Sci.* **2011**, *108*, 4737-4742).

The distance between two anions cannot be immediately obtained from the energy transfer rate constant $k_{SCN^- \rightarrow S^{13}C^{15}N^-}$ yet, because $k_{SCN^- \rightarrow S^{13}C^{15}N^-}$ determined from the experiments is the total rate constant from one donor to all acceptors in one cluster. The size of the cluster needs to be determined in order to convert $k_{SCN^- \rightarrow S^{13}C^{15}N^-}$ into the rate constant from one donor to one acceptor.

4.2 Cluster Size Revealed by Resonant Energy Transfer

The resonant energy transfer method is used to determine the cluster size. As mentioned in the experimental section, on one hand, both the resonant energy transfer from one donor to any acceptor and molecular rotations can cause the anisotropy of vibrational excitation to decay. On the other hand, acceptors can also transfer energy back to the original donor, leading to the recovery of the anisotropy. The probability of reverse transfer is approximately inversely

proportional to the number of acceptors. Therefore, slower energy-transfer-induced anisotropy decays are observed in smaller clusters in which fewer energy acceptors are available for one donor (under our experimental condition, no more than one anion, which is the original energy donor in one cluster, is excited by the laser in the majority of the clusters). Based on this physical picture, a kinetic model is developed to analyze the resonant energy transfer kinetics for the 10M aqueous solution:^{29,30}

$$\frac{R(t)}{R(0)} = e^{-\frac{t}{\tau_{or}}} \left\{ \left[1 - \frac{1}{1 + (n_{tot} - 1) \times c} \right] e^{-[1 + (n_{tot} - 1) \times c] \frac{t}{\tau}} + \frac{1}{1 + (n_{tot} - 1) \times c} \right\}, \quad (3)$$

where τ_{or} is the molecular rotational time constant of $S^{13}C^{15}N^-$ in a cluster, c is the fraction of $S^{13}C^{15}N^-$ (the energy carrier) among all the anions in the solution, n_{tot} is the number of anions (both $S^{13}C^{15}N^-$ and SCN^-) in an energy transfer unit, and τ is the resonant one-donor-to-one-acceptor energy transfer time constant. We experimentally determined $\tau_{or} = 10 \pm 1.0 ps$ from the anisotropy measurement of the 1% $KS^{13}C^{15}N$ 10M aqueous solution (Fig.3). Therefore, only two parameters (τ and n_{tot}) are experimentally unknown. Experimental resonant acceptor concentration dependent anisotropy decay of the $^{13}C^{15}N$ stretch pump/probe signal of $S^{13}C^{15}N^-$ in 10M aqueous solutions with different $KS^{13}C^{15}N/KSCN$ molar ratios is displayed in Fig.3. In a solution with very few resonant acceptors, e.g. the 1:99 solution, the anisotropy decay is slow. In a solution with many resonant acceptors available, e.g. the 100:0 solution, the anisotropy decay is fast. Calculations with the two adjustable parameters simultaneously well fit the experimental results of six different isotope ratios (Fig.3). The two parameters were obtained as $\tau = 54 \pm 8 ps$ and $n_{tot} = 18 \pm 3$, indicating that about 18 anions are involved in an effective energy transfer unit within a cluster. It is worthwhile to emphasize that a large cluster can contain more than one

energy transfer unit. Only in dilute solutions where clusters are smaller, the size of an energy transfer unit is identical to a cluster.

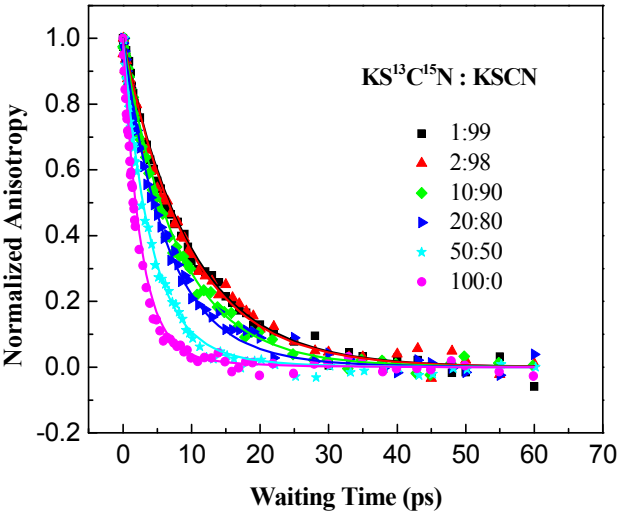


Figure 3. The anisotropy decay data (dots) of the $^{13}\text{C}^{15}\text{N}$ stretch pump/probe signal of $\text{S}^{13}\text{C}^{15}\text{N}^-$ in 10M aqueous solutions with different $\text{KS}^{13}\text{C}^{15}\text{N}/\text{KSCN}$ molar ratios. Lines are calculated from Eq.1.²⁹ Reprinted with permission from Reference 29 (Bian, H.; Wen, X.; Li, J.; Chen, H.; Han, S.; Sun, X.; Song, J.; Zhuang, W.; Zheng, J. Ion Clustering in Aqueous Solutions Probed with Vibrational Energy Transfer. *Proc. Nat. Acad. Sci.* **2011**, *108*, 4737-4742).

4.3 Average Anionic Distance Determined from both Nonresonant and Resonant Energy Transfers

From both nonresonant vibrational energy exchange and resonant energy transfer induced anisotropy decay measurements, the energy transfer time constants from one donor to all possible acceptors for the 10M $\text{KSCN}/\text{KS}^{13}\text{C}^{15}\text{N} \sim 1/1$ aqueous solution are determined to be $1/k_{0\text{ cm}^{-1}} = 6\text{ ps}$ for the energy gap $\Delta\omega_{DA} = 0\text{ cm}^{-1}$ and $1/k_{75\text{ cm}^{-1}} = 115\text{ ps}$ for the energy gap $\Delta\omega_{DA} = 75\text{ cm}^{-1}$. According to eq.1 and these two energy transfer time constants, the total

coupling $V_{DA-one-to-all}$ is determined to be 4.1 cm^{-1} and the dephasing line width is 15 cm^{-1} .³²

The one-donor-to-one-acceptor coupling is $V_{1 \rightarrow 1} = V_{DA-one-to-all} / \sqrt{9} = 1.4 \text{ cm}^{-1}$ where 9 is the number of resonant acceptors in the 1/1 solution which is 50% of 18 - the number of total anions n_{tot} in the 10M pure KSCN solution.^{30,32} The D/A distance $r_{DA} = 5.1 \text{ \AA}$ is then obtained from $V_{1 \rightarrow 1} = 1.4 \text{ cm}^{-1}$ and eq.2 with parameters: $n = 1.5$, $\mu_D = \mu_A = 0.33D$, $\langle \kappa \rangle = \sqrt{2/3}$.³² This distance is larger than the shortest anionic distance in the KSCN crystal ($4.0 \text{ \AA}$), but smaller than the nominal anionic distance ($5.6 \text{ \AA}$) of the solution if ion clustering doesn't occur. This is because the determined distance from energy transfer experiments is the average distance from one donor to all possible acceptors at different distances. Surrounding one anion in the KSCN crystal³³, four closest anions exist at a distance of $4.0 \text{ \AA}$. The next two anions have distances of $4.8 \text{ \AA}$, and then two at $5.6 \text{ \AA}$, and so on. Therefore, within an energy transfer unit with 18 anions in the 10M solutions, some anions must be located at distances much longer than the shortest $4.0 \text{ \AA}$ because of the geometric constraint. In order to examine whether the closest anionic distance in an ion cluster in aqueous solutions is the same as that in the crystal, what we need is to measure the distance in a cluster with no more than four anions. This is experimentally achievable. Required by chemical equilibrium, the ion clusters must become smaller and fewer in a more dilute KSCN solution.

4.4 Anionic Distance in a Small Cluster Is the Same as in the Crystal

Both nonresonant and resonant vibrational energy transfers among the nitrile stretches are measured in the potassium thiocyanate aqueous solutions of different concentrations.²⁹ Fig.4 displays the concentration dependence of the 2D IR spectra of 1/1 KSCN/KS¹³C¹⁵N aqueous solutions at three different waiting times.²⁹ As we can see, at the same waiting time, e.g. 50 ps,

the vibrational energy exchange cross peaks are smaller for a more dilute solutions. This indicates that the vibrational energy exchange is slower in a relatively dilute solution.

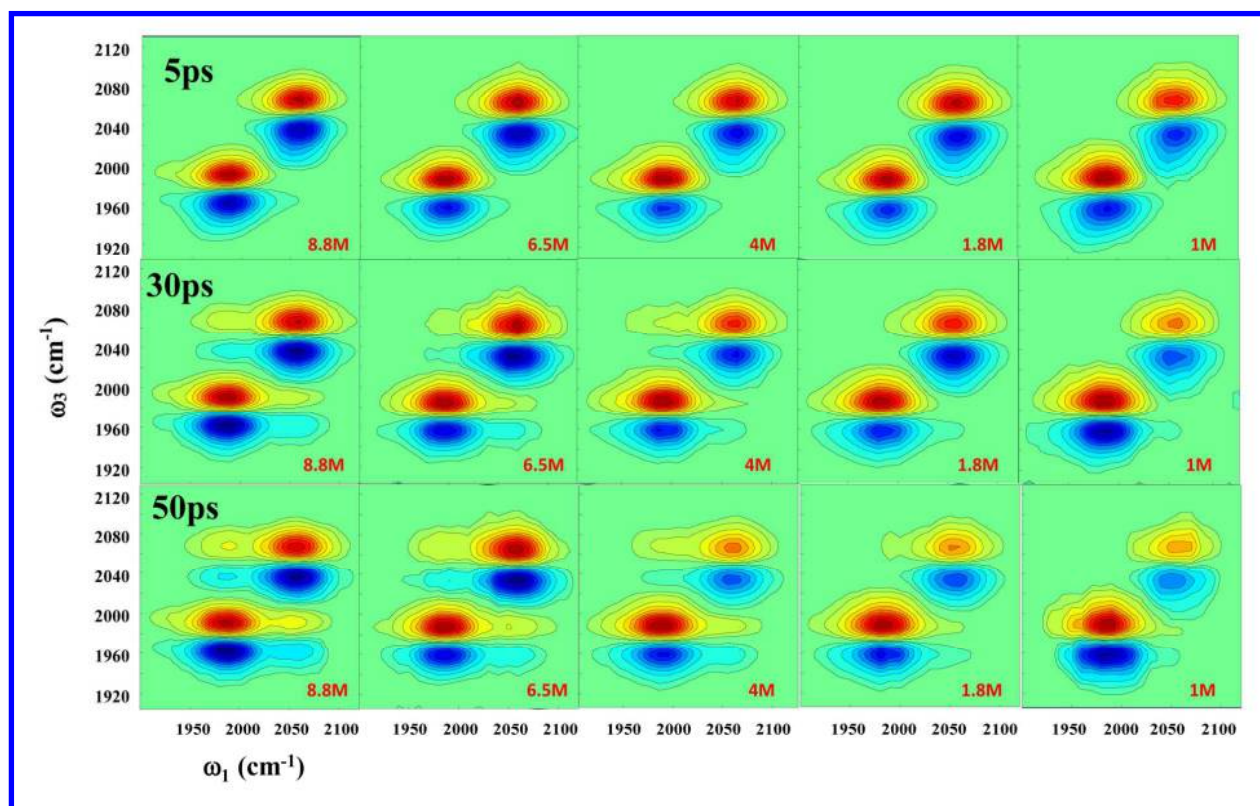


Figure 4. The 2D IR spectra of 1:1 KSCN/KS¹³C¹⁵N aqueous solutions with different concentrations at three different waiting times.²⁹ Reprinted with permission from Reference 29 (Bian, H.; Wen, X.; Li, J.; Chen, H.; Han, S.; Sun, X.; Song, J.; Zhuang, W.; Zheng, J. Ion Clustering in Aqueous Solutions Probed with Vibrational Energy Transfer. *Proc. Nat. Acad. Sci.* **2011**, *108*, 4737-4742).

Quantitative analyses on both nonresonant and resonant energy transfer data based on the procedure developed for the 10M solutions show that fewer and smaller ion clusters form in a more dilute solution. The results are listed in table 1.^{29,32} In the 1M and 1.8M solutions, the ion cluster contains only three to four anions. Therefore, the average D/A distance in these small clusters determined by the energy transfer method must be very close to the shortest anionic

distance in the clusters. In the 1M and 1.8M solutions, the one-donor-to-one-acceptor couplings $V_{1 \rightarrow 1}$ are determined to be 2.5 cm^{-1} and 2.3 cm^{-1} , respectively. The D/A distances determined from these two coupling strengths and eq.2 are 4.3 Å and 4.4 Å, very close to the shortest anionic distance 4.0 Å in the KSCN crystal.

Table 1. *Experimental and MD simulation results of the cluster percentage, the number of anions (n_{tot}) in an energy transfer unit and the energy donor-acceptor distances r_{DA} in KSCN aqueous solutions at different concentrations.*^{29,32}

	Experimental Cluster percentage	MD Cluster percentage	n_{tot}	r_{DA} (Å)
KSCN (10M)	$95 \pm 1\%$	99.7%	18 ± 3	5.1
KSCN (8.8M)	$92 \pm 1\%$		13 ± 2	5.0
KSCN (6.5M)	$70 \pm 4\%$		9 ± 2	4.8
KSCN (4M)	$67 \pm 4\%$	79.5%	5 ± 2	4.6
KSCN (1.8M)	$35 \pm 5\%$	31.4%	4 ± 1	4.4
KSCN (1M)	$27 \pm 6\%$		3 ± 1	4.3

4.5 The Shortest Anionic Distance in the Crystal Determined by the Energy Transfer Method is the Same as XRD Result

To our knowledge, no other experimental techniques exist which can determine the anionic distances within the ion clusters in potassium thiocyanate aqueous solutions. Because of this, from an experimental point of view, we cannot immediately conclude that the anionic distances determined by the vibrational energy transfer method described above are reliable, though the experimental distances are close to those from MD simulations.^{29,31} To benchmark the vibrational energy transfer method, we require a sample in which the D/A distances can be

characterized by other mature techniques, e.g. XRD. Accordingly, we measured both the resonant and nonresonant vibrational energy transfers among the nitrile stretches in the KSCN isotope mixed crystals.³³ In the KSCN crystal, the relative orientations and distances among the thiocyanate anions have been well characterized with XRD and neutron scattering.^{32,55} The two shortest anionic distances are 4.02 Å and 4.03 Å, as displayed in Fig.5.

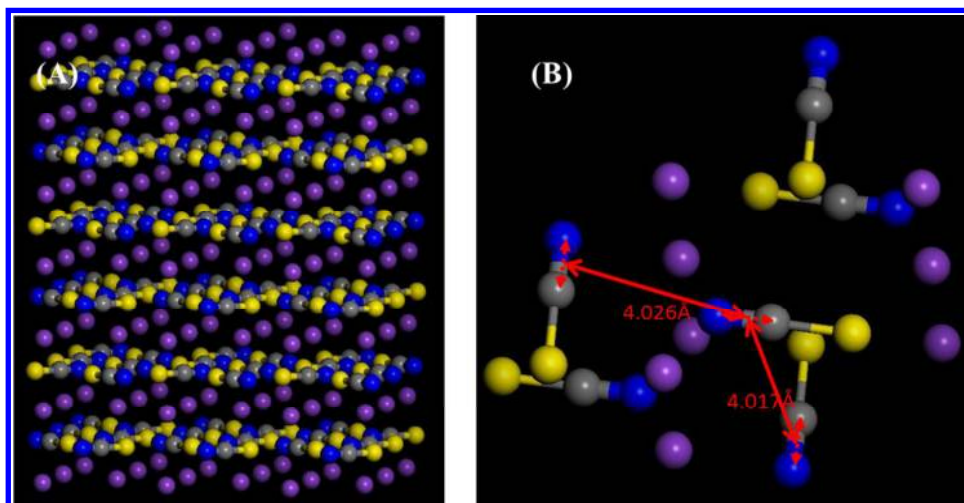


Figure 5. Crystalline structure of KSCN crystal: (A) a full view; (B) a zoomed-in structure highlighting the two shortest anionic distances. K (purple), S (yellow), C (gray), and N (blue). Reprinted with permission from Reference 33 (Chen, H.; Wen, X.; Li, J.; Zheng, J. Molecular Distances Determined with Resonant Vibrational Energy Transfers. *J. Phys. Chem. A* **2014**, *118*, 2463-2469). Copyright 2014 American Chemical Society.

Resonant acceptor concentration dependent anisotropy decay experiments are conducted on the potassium thiocyanate crystals with different $\text{KS}^{13}\text{C}^{15}\text{N}/\text{KSCN}$ molar ratios. The results are displayed in Fig.6.³³ The results are similar to those of the 10M solutions in Fig.3, with the exception that the anisotropies measured in the crystals (see Fig.6) do not decay to zero because the rotations in the crystals are hindered and the relative orientations of the anions are not random.³³ Analyzing the anisotropy decay data with a kinetic model that accounts for all possible

vibrational energy transfer pathways and molecular wobbling in the crystal show that the resonant energy transfer time between two closest anions in the crystals is $1/k_{01} = 27 \pm 3$ ps. Combining this energy transfer time with the nonresonant energy transfer results,^{32,33} the distance between two closest anions in the KSCN crystal is determined to be $r_{DA} = 3.9 \pm 0.3$ Å, which is identical to that determined by XRD within the experimental uncertainty.³³ Calculations based on the monopole theory show that the point dipole approximation used in the method causes only negligible uncertainty in the distance determined. This is because the D/A distance is about three times larger than that of the CN bond length.³³

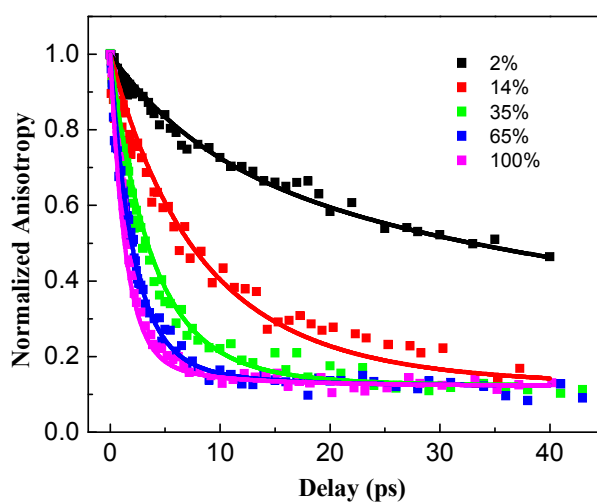


Figure 6. Waiting time dependent anisotropies of KSCN/KS¹³C¹⁵N mixed crystals with different molar percentages of resonant energy donor species at room temperature. Dots represent experimental results, and curves are calculated results. Each percentage value in the legend represents the percentage of resonant energy acceptors in each sample. Reprinted with permission from Reference 33 (Chen, H.; Wen, X.; Li, J.; Zheng, J. Molecular Distances Determined with Resonant Vibrational Energy Transfers. *J. Phys. Chem. A* **2014**, *118*, 2463-2469). Copyright 2014 American Chemical Society.

The resonant energy transfer experiments confirm the validity of the energy transfer method as an “angstrom molecular ruler”. At this stage, one point must be emphasized. In the crystals, the nonresonant energy transfers in which the phonon compensation mechanism plays an important role cannot be used as they are in liquids to determine the D/A distance with eq.1. This is because the energy transfer equation for the phonon compensation is very difficult to be quantified and quite different from eq.1.³² Although the nonresonant vibrational energy transfer time in the KSCN/KS¹³C¹⁵N=1/1 mixed crystal ($1/k_{SCN^- \rightarrow S^{13}C^{15}N^-} = 99 ps$) is almost the same as that of its saturated aqueous solution ($1/k_{SCN^- \rightarrow S^{13}C^{15}N^-} = 115 ps$), we consider this similarity as a coincidence rather than clear evidence to support ion clustering in the solutions because the energy transfer mechanisms in the crystals are distinct from the solutions.³² In fact, because of the different mechanisms, the energy transfers of the same donors and acceptors in crystals and in liquid solutions may depend on the energy gap in opposing ways. Such an example is displayed in Fig.7.⁴⁸ Fig.7A&B display the 0-1 transition portions of 2D IR spectra of the KSCN/KS¹³CN=1/1 DMF 1/8 solution (gap $\sim 48 cm^{-1}$) and the KSCN/KS¹³C¹⁵N=1/1 DMF 1/8 solution (gap $\sim 75 cm^{-1}$) at a waiting time of 50 ps at room temperature. In the solutions, the energy transfers are governed by the dephasing mechanism (eq.1). Therefore, the energy transfer is slower with a larger gap. This is confirmed by that the energy transfer cross peaks 5&7 are smaller with a larger gap (fig.7B). On the contrary, the phonon compensation mechanism dominates the energy transfers in the mixed crystals at 80K (fig.7C&D).³² In the mixed crystals, the phonon density at $75 cm^{-1}$ is much larger than that at $50 cm^{-1}$.⁴⁸ The energy transfer is faster with a larger gap because of the larger phonon density, resulting in larger energy transfer cross peaks 5&7 (fig.7D).

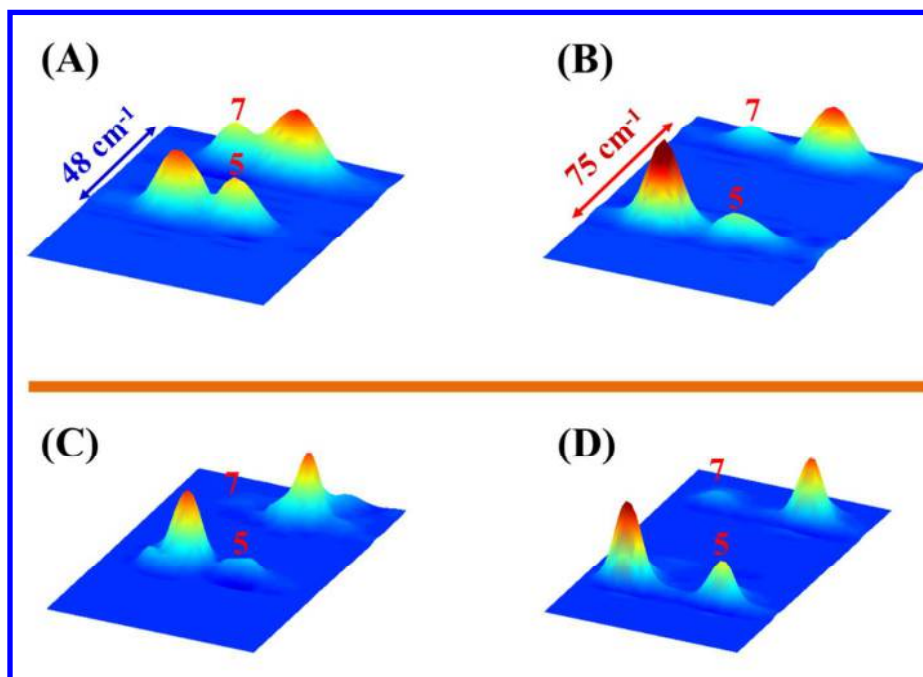


Figure 7. 2D IR spectra of (A) the KSCN/KS¹³CN=1/1 DMF solution (energy gap ~ 48 cm⁻¹) and (B) the KSCN/KS¹³C¹⁵N=1/1 DMF solution (energy gap ~ 75 cm⁻¹) at a waiting time of 50 ps at room temperature. 2D IR spectra of (C) a KSCN/KS¹³CN=1/1 mixed crystal (energy gap ~ 48 cm⁻¹) and (D) a KSCN/KS¹³C¹⁵N=1/1 mixed crystal (energy gap ~ 75 cm⁻¹) at a waiting time of 150 ps at 80K. Only the 0-1 transition signals are plotted in all the figures. Reprinted with permission from Reference 48 (Chen, H.; Zhang, Q.; Guo, X.; Wen, X.; Li, J.; Zhuang, W.; Zheng, J. Nonresonant Energy Transfers Independent on the Phonon Densities in Polyatomic Liquids. J. Phys. Chem. A 2014, DOI: 10.1021/jp511651t, in press). Copyright 2014 American Chemical Society.

4.6 Cation Involved in Ion Clustering

All the conclusions about ion clusters in aqueous solutions mentioned above are solely determined from the anion measurements. No information is available for the cation K⁺ because it does not produce any vibrational signal. Therefore, from the experimental results presented above, it is not clear whether the cation is involved in the ion clustering. Although, in principle,

it should be involved in order to neutralize the charge in the clusters. In order to address this issue, we use NH_4^+ to replace K^+ so that the cation NH_4^+ can also generate a vibrational signal. In a NH_4SCN aqueous solution, we can measure the energy transfers not only between the anion and water, but also between the anion and cation. This allows us to directly determine if cations bind to anions in the solution.³⁴ Fig.8 displays the 2D IR spectra of a $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution. The diagonal peak pairs 1'&2', 3'&4', 5'&6' belong to the 0-1&1-2 transitions of the CN stretch of SCN^- anion, the OH bending of the water molecule, and the NH bending of the NH_4^+ cation, respectively. The vibrational energy transfer from CN stretch to OH bending and the heat-induced OH bending absorption change contribute to both cross peak pairs 7'&8'. Cross peak pairs 9'&10' arise from: (1) the vibrational coupling between the CN stretch and the NH bending, (2) the vibrational energy transfer from the CN stretch to the NH bending, (3) the vibrational coupling between a combination band of NH_4^+ at $\sim 2060\text{ cm}^{-1}$ and the NH bending, (4) the vibrational energy transfer from the combination band of NH_4^+ to the NH bending, and (5) the heat-induced NH bending absorption change. Cross peak pairs 11'&12' are from (1) the vibrational coupling between the NH bending and the OH bending, (2) the vibrational energy transfer from the OH bending to the NH bending, and (3) the heat-induced NH bending absorption change. After properly removing the contributions from the heat effect and the vibrational coupling, quantitative analyses on the energy transfer kinetics presented in Fig.8 show that 49% of the CN excitation transfers to the OH bending, and 44% transfers to the NH bending. The decrease of the CN/OH energy transfer efficiency (49%) compared with that in a $\text{KSCN}/\text{H}_2\text{O}$ 1/10 solution (90%) indicates that, NH_4^+ directly competes with water to bind to SCN^- . Nearly one half of the H_2O molecules of the $\text{SCN}^-/\text{H}_2\text{O}$ binding sites in the KSCN solution are replaced by the NH_4^+ cations in the NH_4SCN solution. Further analyses on results in

two relatively dilute (1/10 and 1/25) solutions show that the average $\text{NH}_4^+/\text{SCN}^-$ binding affinity (compared to that of $\text{H}_2\text{O}/\text{SCN}^-$) is determined to be $K = 18 \pm 4$. As a result, $\sim 60\%$ of the NH_4^+ cations directly bind to the SCN^- anions in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution.³⁴ This value is very close to the ion clustering ratio - 67% of the SCN^- anions in a $\text{KSCN}/\text{D}_2\text{O}$ (1/10) solution associated with other anions determined by measuring the nonresonant vibrational energy transfer among the SCN^- and $\text{S}^{13}\text{C}^{15}\text{N}^-$ anions. Although K^+ and NH_4^+ have different properties and the definitions of ion associations in the two experiments are not exactly the same, the similarity between the cation/anion association ratio 60% and anion/anion association ratio 67% may suggest that the anion/cation ratio in an ion cluster is close to 1/1.

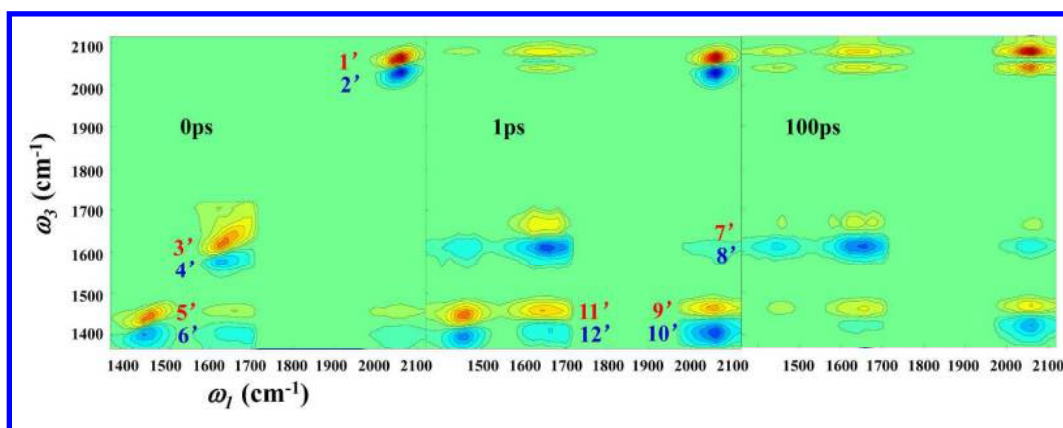


Figure 8. Waiting time dependent 2D IR spectra of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution. Reprinted with permission from Reference 34 (Li, J.; Bian, H.; Chen, H.; Wen, X.; Hoang, B.; Zheng, J. Ion Association in Aqueous Solutions Probed through Vibrational Energy Transfers among Cation, Anion and Water Molecules. *J. Phys. Chem. B* **2012**, *117*, 4274-4283). Copyright 2012 American Chemical Society.

4.7 The Effects of Cations on Ion Clustering

As discussed above, cations are involved in the ion clustering. This is consistent with MD simulations, which also suggest that cations with different properties may affect ion pairing and

clustering.^{19,56} To further explore the function of the cation in ion clustering, we investigate the vibrational energy transfers among the nitrile stretches in the MSCN/MS¹³C¹⁵N aqueous solutions with M = Li⁺, Na⁺, K⁺, and Cs⁺. The ion cluster concentrations and sizes derived from the measurements are displayed in Fig.9. As displayed in Fig.9, in the 4M solution with the smallest cation Li⁺, about 50% of the anions form clusters containing ~4 anions on average. In a solution with a large cation, more and larger clusters form relative to a solution with a smaller cation. In the solution with the biggest cation Cs⁺, about 70% of the anions form clusters containing ~9 anions. This observation can be explained with the theory of “matching cation and anion sizes”.^{56,57} Briefly, small-small and large-large cation-anion pairs easily associate, while small-large cation-anion pairs easily dissociate. Since SCN⁻ is large and polarizable, it is easier to associate with the large and polarizable Cs⁺ over the small Li⁺.

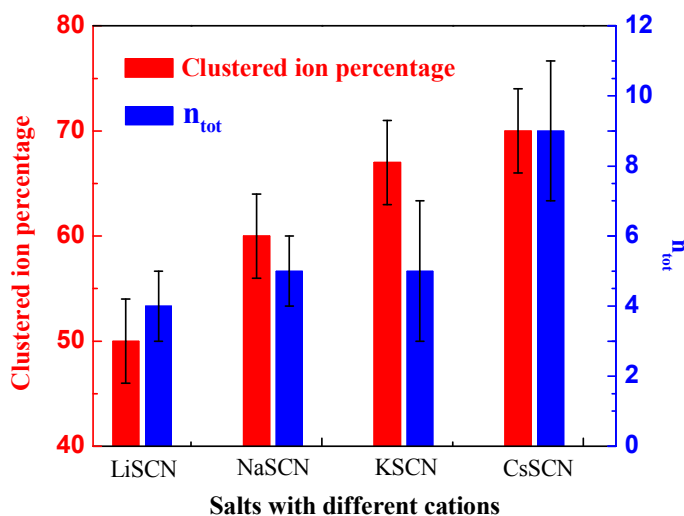


Figure 9. The cation dependence of the ion cluster percentage and the number of anions (n_{tot}) in an energy transfer unit of 4M aqueous solutions of LiSCN, NaSCN, KSCN, and CsSCN.²⁹

Reprinted in part with permission from Reference 29 (Bian, H.; Wen, X.; Li, J.; Chen, H.; Han,

S.; Sun, X.; Song, J.; Zhuang, W.; Zheng, J. Ion Clustering in Aqueous Solutions Probed with Vibrational Energy Transfer. *Proc. Nat. Acad. Sci.* **2011**, *108*, 4737-4742).

4.8 The Clusters are more Melt-Like than Crystal-Like

As introduced above, there are several similarities between ion clusters in the KSCN aqueous solutions and the KSCN crystal: (1) The nonresonant energy transfer times from SCN^- to $\text{S}^{13}\text{C}^{15}\text{N}^-$ are very similar in both the saturated aqueous solution and the crystal (115ps vs. 99ps); (2) the SCN^- anions rotate with the same reorientational time constant ($\tau_{or} \approx 11 \pm 1 \text{ ps}$) in both the saturated aqueous solution and the crystal; (3) the number of anions ($n_{tot} = 18$) in an effective energy transfer unit in the saturated aqueous solution is equal to the number of the first shell SCN^- anions in the crystal of any anion; and (4) the closest anion distance in the ion clusters is the same as the closest anionic distance in the KSCN crystal ($r_{DA} \approx 4.0 \pm 0.4 \text{ \AA}$). However, all these similarities do not imply that the structure of the clusters looks like that of the crystal. In fact, MD simulations predict that the clusters in the solutions look more like a melt, as shown in Fig.10A.²⁹ Fig.10A is a snapshot from the MD simulation of a 10M KSCN aqueous solution. Water molecules are removed to more clearly display the cluster structures. Very different from the crystal (Fig.10B), the relative orientations of the anions in the clusters are random. No long range order is observed in the clusters, which is characteristic of a melt. In addition, the structure in Fig.10A depicts several empty channels interconnecting through the clusters. These empty channels are actually where the water molecules reside. The structure indicates that the ion clusters and water form some sort of microphase-separated interconnected network.

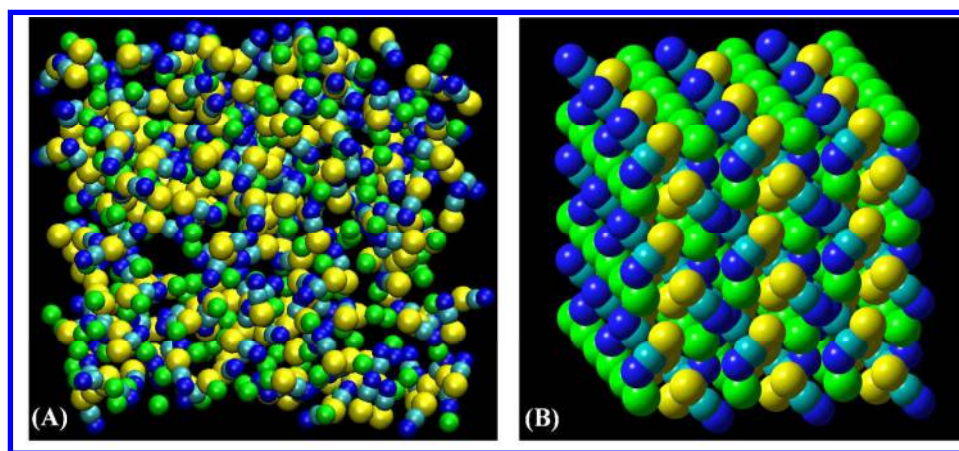


Figure 10. (A) A snapshot from MD simulation for a 10M KSCN aqueous solution. Water molecules are removed to more clearly show the structures of the ion clusters. (B) KSCN crystalline structure. C (light blue), N (deep blue), K (green) and S (yellow).

While the structure depicted in Fig.10A does not necessarily contradict the similar properties between the ion clusters and crystal mentioned above, there are additional experimental results supporting the predicted melt-like cluster structure: (1) the CN excitation signal anisotropy can decay to zero in the aqueous solutions (Fig.3) but it cannot decay to zero in the crystal (Fig.6), indicating that the orientations of anions in the solutions are random but those in the crystal are not. (2) The vibrational frequencies of the CN stretch in concentrated aqueous solutions are close to those of the melts rather than those of the crystals. Fig.11 shows the central frequencies of (A) the OD and (B) the CN stretches in MSCN ($M = \text{Li, Na, K, Cs}$) aqueous solutions of different concentrations.²⁶ The CN stretch frequencies of SCN^- in molten MSCN salts and in the crystals are displayed respectively at the assumed concentration of 25 mol/kg and 30 mol/kg in Fig.11B.^{26,58-60} In Fig.11A, the OD frequencies blueshift in solutions with a higher concentration, independent of the cations. This is probably because the OD frequencies are mainly determined by the number of the anions rather than that of the cations as the anions can directly form H-bonds with the OD but the cations can only interact with the electron pairs of O.

In contrast, the CN stretch frequency of the anion SCN^- is highly dependent on the cations. As displayed in Fig.11B, with increasing concentration, the CN stretch frequency in each MSCN solution approaches that of the corresponding melt, but not that of the corresponding crystal.

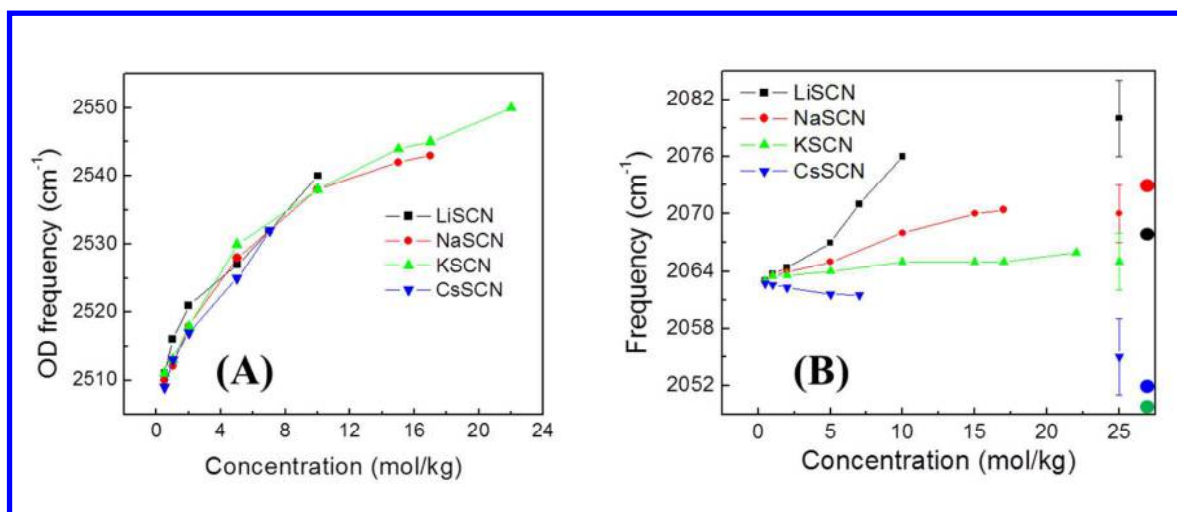


Figure 11. Central frequencies of (A) OD and (B) CN stretches in all MSCN ($M = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) aqueous solutions. The frequencies at 25 mol/kg in (B) are for the molten salts and at 30 mol/kg in (B) are for the crystals (the LiSCN crystal is hydrated). Adapted with permission from Reference 26 (Bian, H.; Chen, H.; Zhang, Q.; Li, J.; Wen, X.; Zhuang, W.; Zheng, J. Cation Effects on Rotational Dynamics of Anions and Water Molecules in Alkali (Li^+ , Na^+ , K^+ , Cs^+) Thiocyanate (SCN^-) Aqueous Solutions. *J. Phys. Chem. B* **2013**, 117, 7972-7984). Copyright 2013 American Chemical Society.

4.9 Consequences of Ion Pairing and Clustering

4.9.1 Different Concentration Dependences of Anion and Water Rotations in the same Solutions

One natural consequence of the structural inhomogeneity (ion clustering) of the electrolyte aqueous solutions is the dynamic inhomogeneity. The dynamic inhomogeneity in the KSCN aqueous solutions can be clearly seen in Fig.12.³¹ Fig.12A&B display the salt

concentration-dependent rotational diffusion time constants (right axis) and viscosities (left axis) of SCN^- anions and D_2O in KSCN aqueous solutions. At lower concentrations, the rotational time constants of both SCN^- and D_2O and viscosity values remain virtually unchanged. With the increase of concentration, the evolutions of rotational dynamics of anions and water are very different. The viscosity gradually increases by about three times from pure water to the saturated solution. Accordingly, the rotation of anions also slows down by about three times (Fig.12A). However, in the same solutions, the water rotation slows down by only about 35% (Fig.12B). The change is significantly smaller than that of SCN^- (~270%).

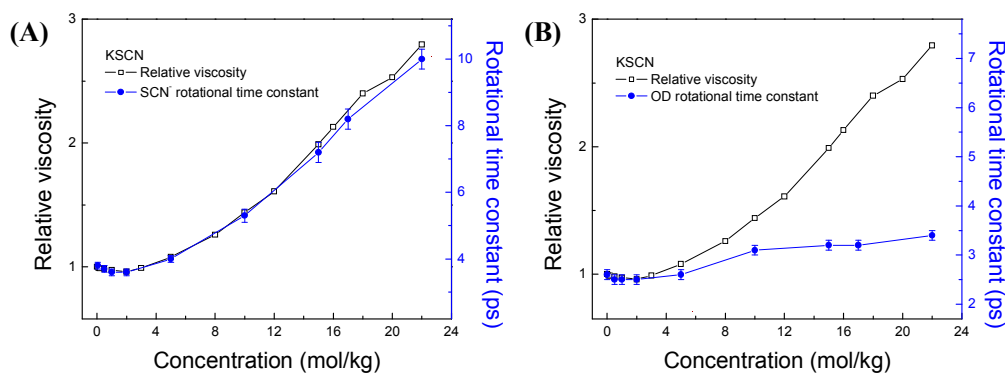


Figure 12. (A) The rotational diffusion time constants of SCN^- anions (blue) and viscosities (black) of KSCN aqueous solutions at different concentrations. (B) The rotational diffusion time constants of D_2O (blue) and viscosities (black) of KSCN aqueous solutions at different concentrations. The unit of concentration is mole (KSCN) per kilogram (water). Reprinted with permission from Reference 31 (Bian, H.; Li, J.; Zhang, Q.; Chen, H.; Zhuang, W.; Gao, Y. Q.; Zheng, J. Ion Segregation in Aqueous Solutions. *J. Phys. Chem. B* **2012**, *116*, 14426-14432). Copyright 2012 American Chemical Society.

The different concentration dependence of the anion and water rotational dynamics within the same solutions can be explained only by the formation of ion clustering. At lower concentrations, the KSCN aqueous solution viscosity drops slightly with the increase of KSCN concentration. This phenomenon is generally attributed to that both K^+ and SCN^- are weakly hydrated. The weak hydration leads to faster molecular motions and a negative B coefficient of the Jones-Dole equation for KSCN aqueous solutions.⁶¹⁻⁶³ Consistent with this explanation, the rotational dynamics of SCN^- anions and water molecules at lower concentrations from 0 to 2 mol/kg slightly speed up with the increase of concentration. At higher concentrations, a substantial fraction of KSCN ions form ion clusters, and the rotation of SCN^- slows down significantly. However, the formation of ion clusters does not affect the water rotational dynamics significantly, as most water molecules are located outside the cluster, in the “bulk” state.

4.9.2 The Dynamic Inhomogeneity is Dependent on Cations

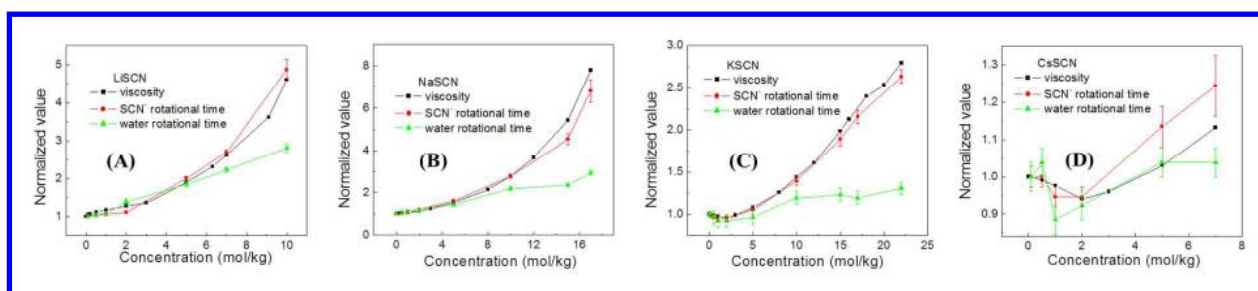


Figure 13. Concentration dependent viscosity, SCN^- rotational time, OD rotational time of (A) LiSCN solution, (B) NaSCN solution, (C) KSCN solution, and (D) CsSCN solution. Reprinted with permission from Reference 26 (Bian, H.; Chen, H.; Zhang, Q.; Li, J.; Wen, X.; Zhuang, W.; Zheng, J. Cation Effects on Rotational Dynamics of Anions and Water Molecules in Alkali (Li^+ , Na^+ , K^+ , Cs^+) Thiocyanate (SCN^-) Aqueous Solutions. *J. Phys. Chem. B* **2013**, *117*, 7972-7984). Copyright 2013 American Chemical Society.

The dynamic inhomogeneity observed in the KSCN aqueous solutions also exists in other MSCN solutions ($M=\text{Li, Na, Cs}$).²⁶ As displayed in Fig.13A~C, in the LiSCN, NaSCN and KSCN solutions, the concentration dependence of the anion rotational time is almost identical to that of the solution viscosity, but the change of the water rotational time with increasing concentration is noticeably smaller, especially at high concentrations. In the CsSCN solutions, limited by its solubility, the measurements can only be conducted at concentrations up to 7 mol/kg. Therefore, the difference in the concentration dependence of anion and water rotations is not as obvious as that in other solutions. However, following the trend of the other cations, it is still perceptible that the anion rotation slows more than the rotation of water at concentrations of 5 and 7 mol/kg.

Two trends in the dynamics shown in Fig.13 are cation dependent. First, in the LiSCN and NaSCN solutions, the anion rotation and the water rotation monotonically slow down with the increase of concentration. However, in the KSCN and CsSCN solutions, they become faster up to 2~3 mol/kg and then slow down with the increase of concentration. As discussed above for the KSCN solutions, the rotational dynamic changes are the sum effect of the weak hydrations of both K^+ and SCN^- which facilitate their rotations and the ion clustering which slow down their rotations.^{26,31,64} All K^+ , Cs^+ , and SCN^- are weakly hydrated, therefore, in both KSCN and CsSCN solutions, faster rotations at low concentrations are observed. In the LiSCN and NaSCN solutions, although SCN^- is still weakly hydrated, both Li^+ and Na^+ are strongly hydrated because of their relatively small sizes and large charge densities. The strong hydrations slow down water rotations. In addition, according to MD simulations, the stronger Na^+ and SCN^- interaction than that between K^+ and SCN^- leads to a slower SCN^- rotation in a Na^+SCN^- ion pair. The slowing effect of Li^+ and Na^+ probably overwhelms the facilitating effect of SCN^- on the

1
2
3 rotational dynamics, resulting in the monotonic rotational slowdown with the increase of
4 concentration displayed in Fig.13A&B.
5
6

7
8 The second cation dependent trend is that the rotations of both water and anions at the
9 same concentrations are slower in a solution with a smaller cation, which will exhibit a larger
10 charge density. For example, at the concentration of 7 mol/kg, the anion rotation in the LiSCN
11 solution is ~2.7 times slower relative to that in more dilute solutions. The corresponding ratio for
12 the NaSCN solution is ~1.9, and for both KSCN and CsSCN solutions is ~1.2. Again, this trend
13 can also be explained with both direct water/cation/anion interactions as well as ion pairing and
14 clustering. In general, a larger charge density leads to a stronger cation/water interaction and a
15 stronger cation/anion interaction, resulting in slower water and anion rotations. However, MD
16 simulations offer another somewhat unexpected explanation for the slower water dynamics in the
17 NaSCN solutions (compared to that of the KSCN solutions). It is not the cation-bound water but
18 the water molecules clamped between cations and anions that are primarily responsible for the
19 slowed overall water rotation.²⁶ The hydration of Na^+ ($\Delta H = -406 \text{ kJ} / \text{mol}$) is stronger than that
20 of K^+ ($\Delta H = -320 \text{ kJ} / \text{mol}$), so more water molecules are brought by Na^+ into the ion clusters in
21 the NaSCN solutions. These water molecules in the ion clusters are the major reason for the
22 overall slow water rotational dynamics that were experimentally observed at high concentrations.
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24 The difference in the relative number of water molecules within the ion clusters in the NaSCN
25 and KSCN solutions is illustrated in Fig.14.
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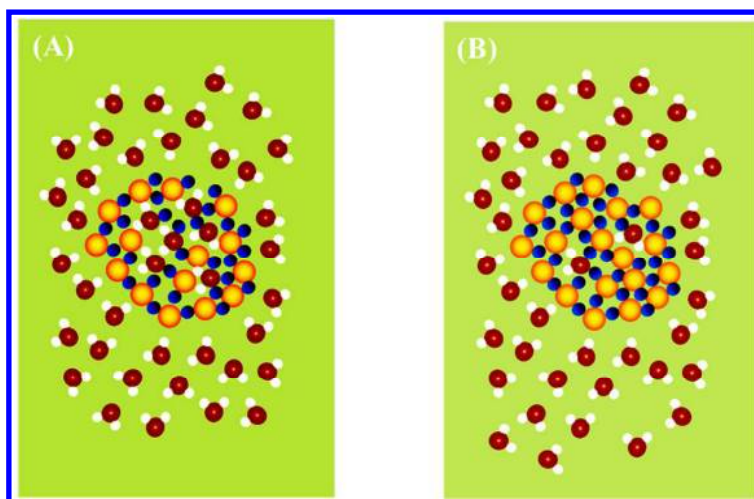


Figure 14. Illustrations of the difference between ion clusters in (A) NaSCN and (B) KSCN aqueous solutions. Water (red and white), cation (blue), anion (yellow). In the ion cluster of the NaSCN solution, more water molecules are confined in the cluster.

4.9.3 Ion Clustering is Dependent on the Nature of Anions and Molecular Additives

The ion/water structural and dynamic inhomogeneity are also observed in aqueous solutions of mixed salts.³¹ Fig.15A&B display the rotational dynamics of ions and water in KSCN aqueous solutions with and without the addition of anions Γ^- (weakly hydrated anion) and F^- (strongly hydrated anion). The rotational dynamics of SCN^- anions in a 5 mol KSCN/kg aqueous solution slows down from 4.2 ± 0.2 ps to 5.8 ± 0.3 ps with the addition of 5 mol KI. However, the addition of KI hardly affects the dynamics of water molecules. The results suggest that Γ^- anions prefer to associate with SCN^- anions rather than water molecules. This conclusion is further confirmed by 2D IR vibrational energy exchange measurements (Fig.15C, D and E). Compared with cross peaks produced by the vibrational energy transfer between SCN^- and $\text{S}^{13}\text{C}^{15}\text{N}^-$ in the (2.5 mol KSCN + 2.5 mol $\text{KS}^{13}\text{C}^{15}\text{N}$)/kg aqueous solution (Peaks 5, 6, 7, and 8 in Fig.15D), the addition of 5 mol KI into the solution produces smaller cross peaks with fewer contours as shown in Fig.15E. It indicates that the addition of KI slows the energy transfers

among the thiocyanate anions. According to the dipole/dipole approximation, slower energy transfers result from the increase of the relative distances among the thiocyanate anions within a cluster. In other words, it indicates that the anion population in close contact (clustered) in the solution decreases with the addition KI. The quantitative calculation results show that³¹ the energy transfer rate slowed by $10\% \pm 2\%$ in Fig.15E. This corresponds to either an increased separation between the SCN^- ions or a $\sim 10\%$ concentration decrease of the closely contacted anions.

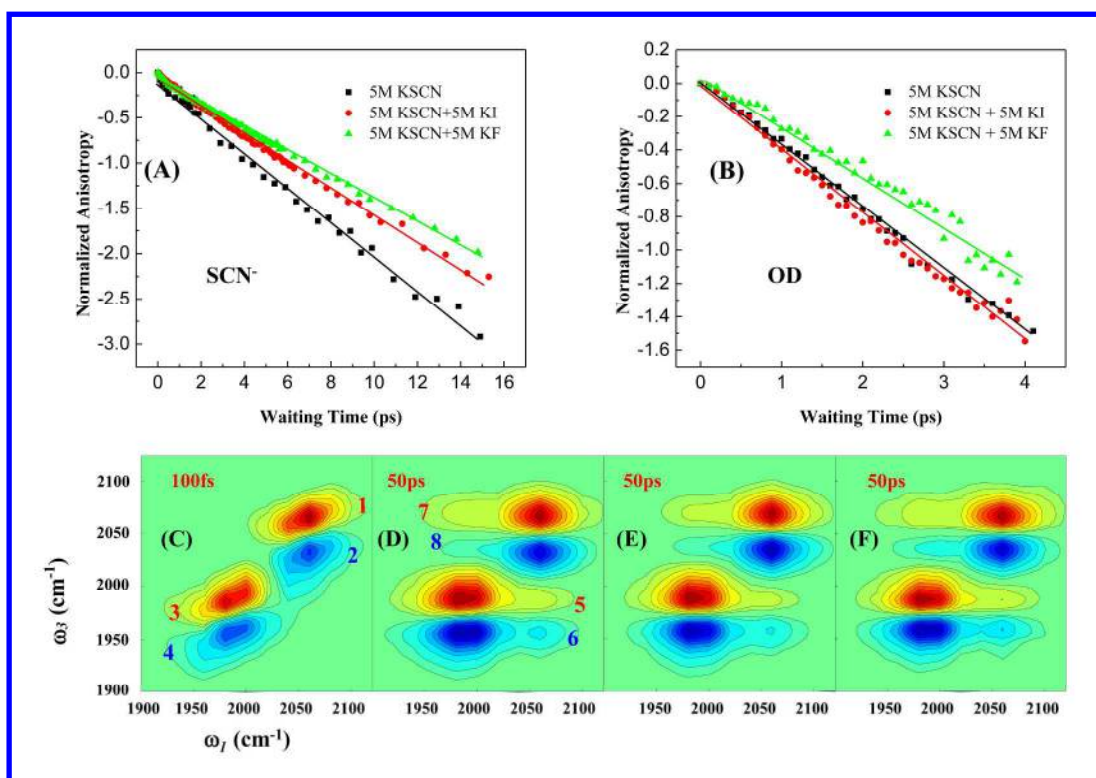


Figure 15. Logarithmic plots of normalized anisotropy dynamics of a (5 mol KSCN+ 5 mol KI)/kg aqueous solution, a (5 mol KSCN)/kg aqueous solution, and a (5 mol KSCN+ 5 mol KF)/kg aqueous solution measured at (A) the SCN^- frequency region and (B) the OD frequency region. All the data are modeled with a single exponential (solid line). (C,D) 2D IR spectra of the (2.5 mol KSCN + 2.5 mol $\text{KS}^{13}\text{C}^{15}\text{N}$)/kg aqueous solution at two waiting times. (E) 2D IR spectrum of the (2.5 mol KSCN + 2.5 mol $\text{KS}^{13}\text{C}^{15}\text{N}$ + 5 mol KI)/kg aqueous solution at 50 ps. (F)

2D IR spectrum of the (2.5 mol KSCN + 2.5 mol $\text{KS}^{13}\text{C}^{15}\text{N}$ + 5 mol KF) /kg aqueous solution at 50 ps. The growth of cross peaks 5, 6, 7, and 8 indicates how fast vibrational energy transfers between SCN^- and $\text{S}^{13}\text{C}^{15}\text{N}^-$. Adapted with permission from Reference 31 (Bian, H.; Li, J.; Zhang, Q.; Chen, H.; Zhuang, W.; Gao, Y. Q.; Zheng, J. Ion Segregation in Aqueous Solutions. *J. Phys. Chem. B* **2012**, 116, 14426-14432). Copyright 2012 American Chemical Society.

In contrast, the addition of 5 mol of KF slows down not only the dynamics of the SCN^- anions, but also the water rotational dynamics. As shown in Fig.15A&B, both water and SCN^- rotations are slowed down respectively from 2.6 ± 0.1 ps to 4.0 ± 0.2 ps and from 4.2 ± 0.2 ps to 7.4 ± 0.3 ps by the addition of KF. Unlike I^- anion that is weakly hydrated, the hydration of F^- is strong.^{65,66} The strong binding between F^- and water leads to a slow water rotation. On the other hand, in the mixed solution, there are not sufficient water molecules to solvate each ion. F^- outcompetes SCN^- for water molecules, reducing the number of water molecules solvating SCN^- anions. As a result, the size and quantity of SCN^- clusters increase with the addition of KF, leading to slower rotational dynamics of SCN^- anions. The formation of more and bigger SCN^- clusters is further supported by the observed faster vibrational energy exchange among anions (Fig.15F), compared to those (Fig.15D) of the solution without the KF addition. This result indicates that the addition of KF facilitates the energy transfer between SCN^- and $\text{S}^{13}\text{C}^{15}\text{N}^-$ anions, contrary to the effect of adding KI to the KSCN aqueous solution.

The above experimental results demonstrate that ions of high water affinities tend to associate with water molecules, reducing the number of water molecules solvating the ion clusters. The effect promotes the formation of more KSCN ion clusters. Additionally, ions of low water affinities tend to associate with the existing clusters. We also observed that other strongly hydrated anions, e.g., CO_3^{2-} and HPO_4^{2-} have similar effects as F^- .³¹ With the addition of CO_3^{2-} or

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3 HPO_4^{2-} , both SCN^- and water rotations slow down and vibrational energy exchanges among
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5 anions become faster. These results indicate that the structures and concentrations of ion clusters
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7 in the KSCN mixed solutions are determined by the nature of the additive anions. Because of the
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9 ion clustering, the local viscosity of SCN^- anions is different from that of the water molecules.
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11 The structural difference results in different rotational dynamics of the two components in the
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13 seemingly homogeneous electrolyte aqueous solutions.
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18 Similarly, adding molecules with different water affinities and SCN^- -binding affinities into
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20 KSCN aqueous solutions also disrupts ion clustering.³⁵ Using this phenomenon, the molecular
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22 mechanism of SCN^- induced protein denaturation is investigated by adding model molecules that
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24 represent the building blocks of proteins into KSCN aqueous solutions. It is found that
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26 thiocyanate anions can directly bind to the charged ammonium group of amino acid in aqueous
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28 solutions. The interactions between the amide groups and SCN^- are also observed. The binding
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30 affinity between the charged amino acid residues and SCN^- is about 20 times bigger than that
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32 between amino acids and water. It is about 5~10 larger than that between the neutral backbone
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34 amide groups and SCN^- . The experiments suggest that the chemical nature of ions and
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36 molecules, rather than the dielectric constant, play a critical role in ion/molecule interactions in
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38 aqueous solutions.
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43 5. Perspectives

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45 Historically, it has long been known that vibrational energy can transfer among different
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47 molecules in a condensed phase.^{52,53,67-72} However, in spite of its obvious advantages over the
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49 electronic energy transfer method: (1) it is free of perturbative labels; (2) its chromophores are
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51 chemical bonds themselves; and (3) its spatial resolution is 0.1~0.2 nm, ten times better than
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53 FRET, intermolecular vibrational energy transfer was never previously used as a molecular ruler.
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There are several practical reasons preventing vibrational energy transfer from being applied to measure molecular distances: (1) For most vibrational modes with frequencies achievable by fs or ps IR lasers ($> 800\text{ cm}^{-1}$), intramolecular vibrational relaxations (a few ps) are typically much faster than intermolecular vibrational energy transfers (tens or hundreds of ps or slower), excluding some strongly H-bonded systems, e.g. water. As a result, intermolecular vibrational energy transfer signals are typically very weak. (2) Resonant energy transfer, the fastest intermolecular vibrational energy transfer, is typically measured with the anisotropy decay method. However, because the anisotropy decay is also caused by molecular rotations which are typically faster than the resonant vibrational energy transfer, it is difficult to quantify the minor contribution from energy transfer to the experimental anisotropy decay signal. (3) The nonresonant vibrational energy transfers in principle could be measured with two-color IR pump/probe or 2D IR or IR/Raman methods by observing the growth of cross peaks. However, even if the energy transfer rate constant could have been quantitatively determined, there were not theories that could have quantitatively converted the rate constant into distance. This is because previous theories about nonresonant vibrational energy transfers were either the correlation formalism³⁷ or the phonon compensation mechanism,⁴⁴ both of which contain parameters that cannot be experimentally quantitatively determined. (4) The vibrational transition dipoles (0.2D~0.4D) are typically more than ten times smaller than those of the electronic transition dipoles. Previously, IR detectors were significantly less sensitive than UV-Vis detectors, and the fs or ps IR lasers were not sufficiently powerful. All these factors imposed tremendous difficulties for the detection of the extremely weak intermolecular nonresonant vibrational energy transfer signals. This is still the case even today. For example, energy can transfer from the CN stretch of $\text{C}_6\text{H}_5\text{SeCN}$ to the C-D stretch of CDCl_3 through the

C₆H₅SeCN...D-CCl₃ H-bond with a gap of only 97 cm⁻¹. However, the signal is so weak that even the most powerful 2D IR technique developed so far, and specifically designed for this purpose, can barely detect it.⁵³

The thiocyanate system studied in this work is special. The nitrile stretch of the thiocyanate anion is among the strongest vibrations in molecular systems. Its vibrational lifetime in D₂O and some organic solvents is tens of ps, almost one order of magnitude longer than the typical vibrational lifetimes in liquids, partially because of the “heavy atom effect” of its S atom.⁵³ Additionally, its vibrational frequencies can be easily tuned by isotope labels. All these properties allow the thiocyanate system to be used as a model system to thoroughly investigate intermolecular vibrational energy transfer in condensed phases and realize the possibility of using intermolecular vibrational energy transfer as an angstrom molecular ruler. Although the methodology and principle laid out from the thiocyanate studies are general for using vibrational energy transfer to measure molecular distances in liquids, we expect the very few other high frequency vibrational modes (> 800 cm⁻¹) can be used for the same purpose because of either their relatively short lifetimes or relatively weak transition dipole moments. Some special vibrational chromophores with long lifetimes and large transition dipole moments may be required in order to use this vibrational energy transfer molecular ruler method, unless the laser techniques or the IR detection methods are tremendously improved so that very weak IR signals can be easily detected. Expanding the laser frequency and detection range to low frequencies, below 800 cm⁻¹, which is achievable^{50,73} can make the vibrational energy transfer method more accessible. In this scenario the vibrational energy of high frequency modes ultimately relaxes to low frequency modes, resulting in energy transfer to other molecules. Another way to apply vibrational energy transfer to measure distances is to use the vibrational relaxation induced heat

effect,^{54,74} in which one high frequency mode on one molecule is used as the energy source and another high frequency mode on another molecule is used as the energy transfer reporter.^{54,75} The energy source mode relaxes its energy to several low frequency modes from which the energy transfers to other low frequency modes on the other molecule. The reporter mode on the other molecule senses the excitations of the low frequency modes from the energy transfer.

In summary, the methodology and principle of the vibrational energy transfer molecular ruler method demonstrated by the thiocyanate system are general, but several intrinsic properties of molecular vibrations and limitations of experimental techniques have restricted its accessibility and applications. However, we believe that with the developments of laser and detection techniques and molecular designs, the vibrational energy transfer method will be more accessible and find more applications beyond thiocyanate or the studies of ion pairing and clustering.

6. Concluding Remarks

In this article, we introduced the principle of intermolecular vibrational energy transfer, the experimental setup, and the procedure to quantitatively obtain the vibrational energy transfer rate and convert the rate constant into the energy donor/acceptor distance in condensed phases. The application of the method to the studies of ion pairing and clustering in strong electrolyte aqueous solutions is demonstrated with MSCN aqueous solutions, where M = Li, Na, K, Cs, and NH₄. The experiments suggest that ions in the concentrated aqueous solutions can form a substantial amount of ion clusters in which both cations and anions are involved. More and larger clusters form in more concentrated solutions, as well as in solutions with a larger cation. In KSCN solutions, the shortest anionic distance in the ion clusters is the same as that in the KSCN crystal. The rotational time of the anion and the nonresonant vibrational energy transfer time

with a gap 75 cm^{-1} in the ion clusters of the KSCN saturated solution are very similar to those in the KSCN crystal. However, the structure of the KSCN ion clusters is very different from the crystalline structure. The ion clusters more closely resemble the melt. They form an interconnected network in the saturated aqueous solution. Because of ion clustering, the dynamics of the anion and water in the same solutions have distinct behaviors. At high concentrations, the anion rotation significantly slows down because of the size increase of ion clusters, but the slowing of water rotation is very modest because many of the water molecules still remain in the “bulk” state due to ion clustering. The rotational dynamics of both water and anions are slower in a solution with a smaller cation. The smaller cation has a larger charge density, causing a stronger cation/anion interaction and cation/water interaction which leads to more water molecules confined in ion clusters. Adding ions or molecules into the KSCN solutions can perturb the ion clusters. Weakly hydrated anions can participate in clustering and form mixed ion clusters with KSCN, while strongly hydrated anions can reduce the effective water molecules solvating KSCN, facilitating the formation of more and large KSCN ion clusters. Similarly, molecules which can strongly bind to SCN^- prefer to participate into the KSCN ion clusters. Molecules which are strongly hydrated prefer to remain hydrated and facilitate the ion clustering of KSCN.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Connors, K. A. *Chemical Kinetics: The Study of Reaction Rates in Solution*; John Wiley & Sons: New York, 1990.
- (2) Pytkowicz, R. M. *Activity Coefficients in Electrolyte Solutions*; CRC Press, Inc.: Boca Raton, Florida, 1979; Vol. 1.
- (3) Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Elsevier Scientific Publishing Company: Amsterdam-Oxford-New York, 1981.
- (4) Gurney, R. W. *Ionic Processes in Solutions*; McGraw-Hill Book Company, Inc.: New York, Toronto, London, 1953.
- (5) Baumgartel, H.; Frank, E. U.; Grunbein, W. *Physical Chemistry of Electrolyte Solutions*; Springer: New York, 1998.
- (6) Bakker, H. J.; Skinner, J. L. Vibrational Spectroscopy as a Probe of Structure and Dynamics in Liquid Water. *Chem. Rev.* **2010**, *110*, 1498-1517.
- (7) Laage, D.; Hynes, J. T. On the Residence Time for Water in a Solute Hydration Shell: Application to Aqueous Halide Solutions. *J. Phys. Chem. B* **2008**, *112*, 7697-7701.
- (8) Moskun, A. C.; Jailaubekov, A. E.; Bradforth, S. E.; Tao, G. H.; Stratt, R. M. Rotational Coherence and a Sudden Breakdown in Linear Response Seen in Room-Temperature Liquids. *Science* **2006**, *311*, 1907-1911.
- (9) Deak, J. C.; Pang, Y.; Sechler, T. D.; Wang, Z.; Dlott, D. D. Real-Time Detection of Vibrational Energy Transfer across a Molecular Layer: Reverse Micelles. *Science* **2004**, *306*, 473 - 476.
- (10) Roberts, S. T.; Petersen, P. B.; Ramasesha, K.; Tokmakoff, A.; Ufimtsev, I. S.; Martinez, T. J. Observation of a Zundel-Like Transition State During Proton Transfer in Aqueous Hydroxide Solutions. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 15154-15159.
- (11) Lin, Y. S.; Auer, B. M.; Skinner, J. L. Water Structure, Dynamics, and Vibrational Spectroscopy in Sodium Bromide Solutions. *J. Chem. Phys.* **2009**, *131*, 144511.
- (12) Moilanen, D. E.; Wong, D.; Rosenfeld, D. E.; Fenn, E. E.; Fayer, M. D. Ion-Water Hydrogen-Bond Switching Observed with 2D IR Vibrational Echo Chemical Exchange Spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 375-380.
- (13) Kropman, M. F.; Bakker, H. J. Dynamics of Water Molecules in Aqueous Solvation Shells. *Science* **2001**, *291*, 2118-2120.
- (14) Sun, Z.; Zhang, W.; Ji, M.; Hartsock, R.; Gaffney, K. J. Contact Ion Pair Formation between Hard Acids and Soft Bases in Aqueous Solutions Observed with 2DIR Spectroscopy. *J. Phys. Chem. B* **2013**, *117*, 15306-15312.

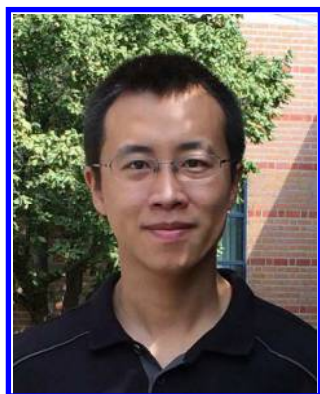
- (15) Ji, M. B.; Odelius, M.; Gaffney, K. J. Large Angular Jump Mechanism Observed for Hydrogen Bond Exchange in Aqueous Perchlorate Solution. *Science* **2010**, *328*, 1003-1005.
- (16) Sherman, D. M.; Collings, M. D. Ion Association in Concentrated NaCl Brines from Ambient to Supercritical Conditions: Results from Classical Molecular Dynamics Simulations. *Geochem. Trans.* **2002**, *3*, 102-107.
- (17) Degreve, L.; da Silva, F. L. B. Structure of Concentrated Aqueous NaCl Solution: A Monte Carlo Study. *J. Chem. Phys.* **1999**, *110*, 3070-3078.
- (18) Hassan, S. A. Computer Simulation of Ion Cluster Speciation in Concentrated Aqueous Solutions at Ambient Conditions. *J. Phys. Chem. B* **2008**, *112*, 10573-10584.
- (19) Chen, A. A.; Pappu, R. V. Quantitative Characterization of Ion Pairing and Cluster Formation in Strong 1 : 1 Electrolytes. *J. Phys. Chem. B* **2007**, *111*, 6469-6478.
- (20) Cerreta, M. K.; Berglund, K. A. The Structure of Aqueous Solutions of Some Dihydrogen Orthophosphates by Laser Raman Spectroscopy. *J. Cryst. Growth* **1987**, *84*, 577-588.
- (21) Rusli, I.; Schrader, G.; Larson, M. Raman Spectroscopic Study of NaNO₃ Solution System-Solute Clustering in Supersaturated Solutions. *J. Cryst. Growth* **1989**, *97*, 345-351.
- (22) Mason, P.; Dempsey, C.; Neilson, G.; Brady, J. Nanometer-Scale Ion Aggregates in Aqueous Electrolyte Solutions: Guanidinium Sulfate and Guanidinium Thiocyanate. *J. Phys. Chem. B* **2005**, *109*, 24185-24196.
- (23) Fitter, J.; Gutberlet, T.; Katsaras, J. *Neutron Scattering in Biology : Techniques and Applications* Springer: Berlin, New York, 2006.
- (24) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; J. Wiley: New York, 1976.
- (25) Marcus, Y.; Hefter, G. Ion Pairing. *Chem. Rev.* **2006**, *106*, 4585-4621.
- (26) Bian, H.; Chen, H.; Zhang, Q.; Li, J.; Wen, X.; Zhuang, W.; Zheng, J. Cation Effects on Rotational Dynamics of Anions and Water Molecules in Alkali (Li⁺, Na⁺, K⁺, Cs⁺) Thiocyanate (SCN⁻) Aqueous Solutions. *J. Phys. Chem. B* **2013**, *117*, 7972-7984.
- (27) Förster, T. *Ann. Phys. Leipzig* **1948**, *2*, 55.
- (28) Scholes, G. D. Long-Range Resonance Energy Transfer in Molecular Systems. *Annu. Rev. Phys. Chem.* **2003**, *54*, 57-87.
- (29) Bian, H.; Wen, X.; Li, J.; Chen, H.; Han, S.; Sun, X.; Song, J.; Zhuang, W.; Zheng, J. Ion Clustering in Aqueous Solutions Probed with Vibrational Energy Transfer. *Proc. Nat. Acad. Sci.* **2011**, *108*, 4737-4742.
- (30) Bian, H.; Chen, H.; Li, J.; Wen, X.; Zheng, J. Nonresonant and Resonant Mode-Specific Intermolecular Vibrational Energy Transfers in Electrolyte Aqueous Solutions. *J. Phys. Chem. A* **2011**, *115*, 11657-11664.
- (31) Bian, H.; Li, J.; Zhang, Q.; Chen, H.; Zhuang, W.; Gao, Y. Q.; Zheng, J. Ion Segregation in Aqueous Solutions. *J. Phys. Chem. B* **2012**, *116*, 14426-14432.
- (32) Chen, H.; Wen, X.; Guo, X. Intermolecular Vibrational Energy Transfers in Liquids and Solids. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13995-14014.
- (33) Chen, H.; Wen, X.; Li, J.; Zheng, J. Molecular Distances Determined with Resonant Vibrational Energy Transfers. *J. Phys. Chem. A* **2014**, *118*, 2463-2469.
- (34) Li, J.; Bian, H.; Chen, H.; Wen, X.; Hoang, B.; Zheng, J. Ion Association in Aqueous Solutions Probed through Vibrational Energy Transfers among Cation, Anion and Water Molecules. *J. Phys. Chem. B* **2012**, *117*, 4274-4283.

- (35) Li, J.; Bian, H.; Wen, X.; Chen, H.; Yuan, K.; Zheng, J. Probing Ion/Molecule Interactions in Aqueous Solutions with Vibrational Energy Transfer. *J. Phys. Chem. B* **2012**, *116*, 12284-12294.
- (36) Petersen, K. A.; Fayer, M. D. Electronic Excitation Transport on Isolated, Flexible Polymer Chains in the Amorphous Solid State Randomly Tagged or End Tagged with Chromophores. *J. Chem. Phys.* **1986**, *85*, 4702-4711.
- (37) Oxtoby, D. W. Vibrational Population Relaxation in Liquids. *Adv. Chem. Phys.* **1981**, *47*, 487-519.
- (38) Knox, R. S.; van Amerongen, H. Refractive Index Dependence of the Förster Resonance Excitation Transfer Rate. *J. Phys. Chem. B* **2002**, *106*, 5289-5293.
- (39) Skinner, J. Vibrational Energy Relaxation of Small Molecules and Ions in Liquids. *Theor. Chem. Acc.* **2011**, *128*, 147-155.
- (40) Nitzan, A.; Mukamel, S.; Jortner, J. Energy Gap Law for Vibrational Relaxation of a Molecule in a Dense Medium. *J. Chem. Phys.* **1975**, *63*, 200-207.
- (41) Rackovsky, S.; Silbey, R. Electronic Energy Transfer in Impure Solids: I. Two Molecules Embedded in a Lattice. *Mol. Phys.* **1973**, *25*, 61-72.
- (42) Leegwater, J. A. Coherent Versus Incoherent Energy Transfer and Trapping in Photosynthetic Antenna Complexes. *J. Phys. Chem.* **1996**, *100*, 14403-14409.
- (43) Fayer, M. D. *Elements of Quantum Mechanics*; Oxford University Press: New York, 2001.
- (44) Kenkre, V. M.; Tokmakoff, A.; Fayer, M. D. Theory of Vibrational Relaxation of Polyatomic Molecules in Liquids. *J. Chem. Phys.* **1994**, *101*, 10618-10629.
- (45) Egorov, S.; Skinner, J. On the Theory of Multiphonon Relaxation Rates in Solids. *J. Chem. Phys.* **1995**, *103*, 1533-1543.
- (46) Holstein, T.; Lyo, S.; Orbach, R. Excitation Transfer in Disordered Systems. In *Laser Spectroscopy of Solids*; Springer: New York, 1986; pp 39-82.
- (47) Dlott, D. D. Vibrational Energy Redistribution in Polyatomic Liquids: 3D Infrared-Raman Spectroscopy *Chem. Phys.* **2001**, *266*, 149-166.
- (48) Chen, H.; Zhang, Q.; Guo, X.; Wen, X.; Li, J.; Zhuang, W.; Zheng, J. Nonresonant Energy Transfers Independent on the Phonon Densities in Polyatomic Liquids. *J. Phys. Chem. A* **2014**, DOI: 10.1021/jp511651t, in press.
- (49) Chen, H.; Bian, H.; Li, J.; Wen, X.; Zheng, J. Ultrafast Multiple-Mode Multiple-Dimensional Vibrational Spectroscopy. *Int. Rev. Phys. Chem.* **2012**, *31*, 469-565.
- (50) Chen, H.; Bian, H.; Li, J.; Guo, X.; Wen, X.; Zheng, J. Molecular Conformations of Crystalline L-Cysteine Determined with Vibrational Cross Angle Measurements. *J. Phys. Chem. B* **2013**, *117*, 15614-15624.
- (51) Chen, H.; Zhang, Y.; Li, J.; Liu, H.; Jiang, D.-E.; Zheng, J. Vibrational Cross-Angles in Condensed Molecules: A Structural Tool. *J. Phys. Chem. A* **2013**, *117*, 8407-8415.
- (52) Bian, H. T.; Wen, X. W.; Li, J. B.; Zheng, J. R. Mode-Specific Intermolecular Vibrational Energy Transfer. II. Deuterated Water and Potassium Selenocyanate Mixture. *J. Chem. Phys.* **2010**, *133*, 034505.
- (53) Bian, H.; Li, J.; Wen, X.; Zheng, J. R. Mode-Specific Intermolecular Vibrational Energy Transfer: I. Phenyl Selenocyanate and Deuterated Chloroform Mixture. *J. Chem. Phys.* **2010**, *132*, 184505.
- (54) Chen, H.; Bian, H.; Li, J.; Wen, X.; Zheng, J. Relative Intermolecular Orientation Probed Via Molecular Heat Transport. *J. Phys. Chem. A* **2013**, *117*, 6052-6065.

- (55) Akers, C.; Peterson, S.; Willett, R. A Refinement of the Crystal Structure of KSCN. *Acta Crystallogr. B* **1968**, *24*, 1125-1126.
- (56) Fennell, C. J.; Bizjak, A.; Vlachy, V.; Dill, K. A. Ion Pairing in Molecular Simulations of Aqueous Alkali Halide Solutions. *J. Phys. Chem. B* **2009**, *113*, 6782-6791.
- (57) Lund, M.; Jagoda-Cwiklik, B.; Woodward, C. E.; Vacha, R.; Jungwirth, P. Dielectric Interpretation of Specificity of Ion Pairing in Water. *J. Phys. Chem. Lett.* **2010**, *1*, 300-303.
- (58) Sathaiah, S.; Sarin, V.; Bist, H. Vibrational Studies of the Structural Phase Transition in Caesium Thiocyanate. *J. Phys.: Condens. Matter* **1989**, *1*, 7829-7841.
- (59) Aliev, A.; Gadzhiev, A. Raman Spectra and Vibrational Relaxation in Molten Thiocyanates. *J. Mol. Liq.* **2003**, *107*, 59-67.
- (60) Baddiel, C.; Janz, G. Molten Thiocyanates: Raman Spectra and Structure. *Trans. Faraday Soc.* **1964**, *60*, 2009-2012.
- (61) Marcus, Y. Effect of Ions on the Structure of Water: Structure Making and Breaking. *Chem. Rev.* **2009**, *109*, 1346-1370.
- (62) Jenkins, H. D. B.; Marcus, Y. Viscosity B-Coefficients of Ions in Solution. *Chem. Rev.* **1995**, *95*, 2695-2724.
- (63) Marcus, Y. The Viscosity B-Coefficient of the Thiocyanate Anion. *J. Chem. Eng. Data.* **2012**, *57*, 617-619.
- (64) Zhang, Q.; Xie, W.; Bian, H.; Gao, Y. Q.; Zheng, J.; Zhuang, W. Microscopic Origin of the Deviation from Stokes-Einstein Behavior Observed in Dynamics of the KSCN Aqueous Solutions: A MD Simulation Study. *J. Phys. Chem. B* **2013**, *117*, 2992-3004.
- (65) Collins, K. D.; Washabaugh, M. W. The Hofmeister Effect and the Behaviour of Water at Interfaces. *Q. Rev. Biophys.* **1985**, *18*, 323-422.
- (66) Zhang, Y. J.; Cremer, P. S. Chemistry of Hofmeister Anions and Osmolytes. In *Annual Review of Physical Chemistry, Vol 61*; Annual Reviews: Palo Alto, 2010; Vol. 61; pp 63-83.
- (67) Hong, X. Y.; Chen, S.; Dlott, D. D. Ultrafast Mode-Specific Intermolecular Vibrational Energy Transfer to Liquid Nitromethane. *J. Phys. Chem.* **1995**, *99*, 9102-9109.
- (68) Laubereau, A.; Kirschner, L.; Kaiser, W. Intermolecular Transfer of Vibrational Energy in Liquids. *Opt. Commun.* **1973**, *9*, 182-185.
- (69) Laubereau, A.; Kaiser, W. Vibrational Dynamics of Liquids and Solids Investigated by Picosecond Light Pulses. *Rev. Mod. Phys.* **1978**, *50*, 607-665.
- (70) Woutersen, S.; Bakker, H. J. Resonant Intermolecular Transfer of Vibrational Energy in Liquid Water. *Nature* **1999**, *402*, 507-509.
- (71) Gaffney, K. J.; Piletic, I. R.; Fayer, M. D. Orientational Relaxation and Vibrational Excitation Transfer in Methanol - Carbon Tetrachloride Solutions. *J. Chem. Phys.* **2003**, *118*, 2270-2278.
- (72) Seifert, G.; Zurl, R.; Patzlaff, T.; Graener, H. Time-Resolved Observation of Intermolecular Vibrational Energy Transfer in Liquid Bromoform. *J. Chem. Phys.* **2000**, *112*, 6349-6354.
- (73) Dai, J.; Xie, X.; Zhang, X. C. Detection of Broadband Terahertz Waves with a Laser-Induced Plasma in Gases. *Phys. Rev. Lett.* **2006**, *97*, 103903.
- (74) Naraharisetty, S. R. G.; Kasyanenko, V. M.; Rubtsov, I. V. Bond Connectivity Measured Via Relaxation-Assisted Two-Dimensional Infrared Spectroscopy. *J. Chem. Phys.* **2008**, *128*, 104502.

(75) Bian, H. T.; Zhao, W.; Zheng, J. R. Intermolecular Vibrational Energy Exchange Directly Probed with Ultrafast Two Dimensional Infrared Spectroscopy. *J. Chem. Phys.* **2009**, *131*, 124501.

Biographies

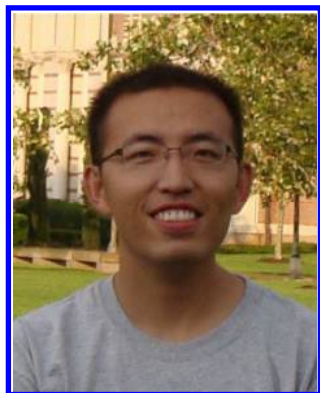


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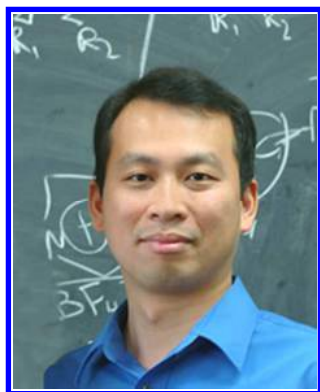


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