

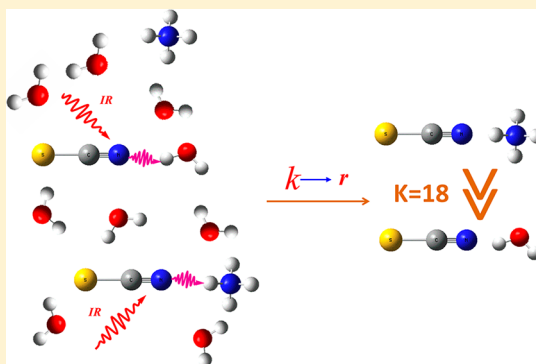
Ion Association in Aqueous Solutions Probed through Vibrational Energy Transfers among Cation, Anion, and Water Molecules

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S Supporting Information

ABSTRACT: KSCN and NH_4SCN aqueous solutions were investigated with intermolecular vibrational energy transfer methods. In a KSCN/ H_2O (1/10 molar ratio) solution, 90% of the initial excitation of the CN stretch ($\sim 2066\text{ cm}^{-1}$) of the SCN^- anion is transferred to the HOH bending mode ($\sim 1636\text{ cm}^{-1}$) of water molecules with an energy transfer time constant 3.1 ps. In a $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10 molar ratio) solution, only 49% of the CN excitation flows to the water HOH bending mode with a time constant 6.3 ps. Most of the remaining CN excitation goes to the NH bending mode ($\sim 1460\text{ cm}^{-1}$) of the NH_4^+ cation with a time constant of 7.0 ps. The results indicate that about 50% of the energy transfer channel from the CN stretch to the HOH bending observed in the KSCN solution is overpowered by the NH_4^+ cations in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ solution. Ion concentration dependent measurements support this argument. According to the dipole/dipole approximation, the CN/OH energy transfer occurs most efficiently between SCN^- anions and the water molecules closest to them. The experimental results therefore suggest that more than 50% of the water molecules closest to the SCN^- anions are replaced by the NH_4^+ cations in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10 molar ratio) solution. The percentage is much larger than the $\text{NH}_4^+/\text{water}$ ratio of 10%, indicating that the ion association between NH_4^+ and SCN^- is caused by the chemical nature of the solution rather than the statistical “forced contact” because of the high ion concentration.



1. INTRODUCTION

A majority of chemical and biological processes in nature occur in aqueous electrolyte solutions.^{1,2} The history of research on the properties of aqueous solutions has been much longer than 100 years.^{3–6} The Debye–Huckel theory is reliable in describing the structures and dynamics for extremely dilute solutions.⁷ However, the theory has difficulties in explaining experimental results at higher concentrations which are commonly found in practical situations, e.g., batteries, fuel cells, salt crystallizations, and the formations of natural mineral compounds. In concentrated solutions, both water/ion interactions and ion/ion interactions play significant roles, and therefore, essentially every problem is a many-body problem. The complexity and practical importance of concentrated electrolyte aqueous solutions have drawn much research interest and also raised many open questions concerning their microscopic structures and dynamics.^{1,3,8–13}

Recently, through vibrational energy transfer measurements, we have found that substantial amounts of ions form ion clusters in the KSCN aqueous solutions of 2–10 M.^{14,15} In the experiments, both nonresonant and resonant energy transfers among the SCN^- and $\text{S}^{13}\text{C}^{15}\text{N}^-$ anions in aqueous solutions were detected at various time delays. From the measured energy transfer kinetics, both the cluster size and the cluster concentration were derived. In addition, the energy transfer rate between SCN^- and $\text{S}^{13}\text{C}^{15}\text{N}^-$ anions in the saturated solution

was found to be the same as that in the potassium thiocyanate crystal at the same temperature (room temperature), further confirming the ion clustering observed in the solutions and the similarity of some properties between the ion clusters and the crystal. However, in these previous experiments, we did not have an internal calibration for the distance between two anions. In other words, we did not use the same method to directly compare the relative distances among the anion, cation, and water molecules in the same solutions to remove the systematic error of the method itself, mainly because the cation K^+ can not provide any detectible vibrational signal in our experiments.

In this work, we used both NH_4SCN and KSCN. In the NH_4SCN aqueous solutions, we were able to measure energy transfers from the CN stretching mode of SCN^- to the NH bending mode of NH_4^+ between the anion SCN^- and the cation NH_4^+ , from the CN stretching mode of SCN^- to the HOH bending mode of water between the anion SCN^- and the water molecules, and from the HOH bending mode to the NH bending mode between the water molecules and the cation NH_4^+ . In the KSCN aqueous solutions, we were able to

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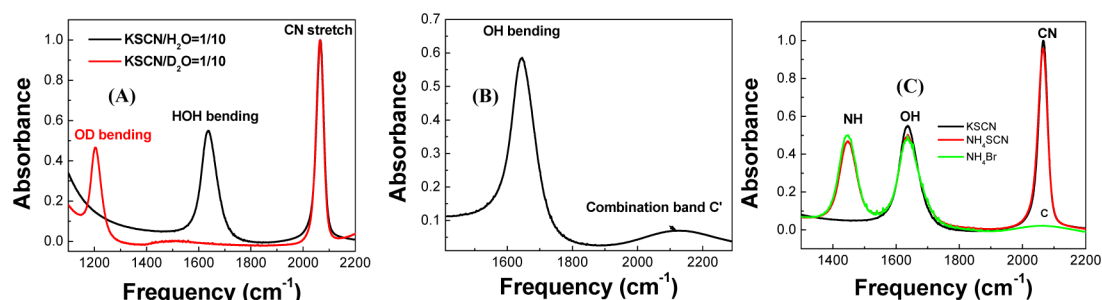


Figure 1. FTIR spectra of (A) KSCN/H₂O (1/10 molar ratio) and KSCN/D₂O (1/10) solutions, (B) pure H₂O, and (C) a NH₄SCN/H₂O (1/10 molar ratio) solution (red), the KSCN/H₂O (1/10) solution (black), and a NH₄Br/H₂O (1/10 molar ratio) solution (green). The thickness of the sample cell is $\sim 3.0 \mu\text{m}$. The CN intensity was normalized to be 1.

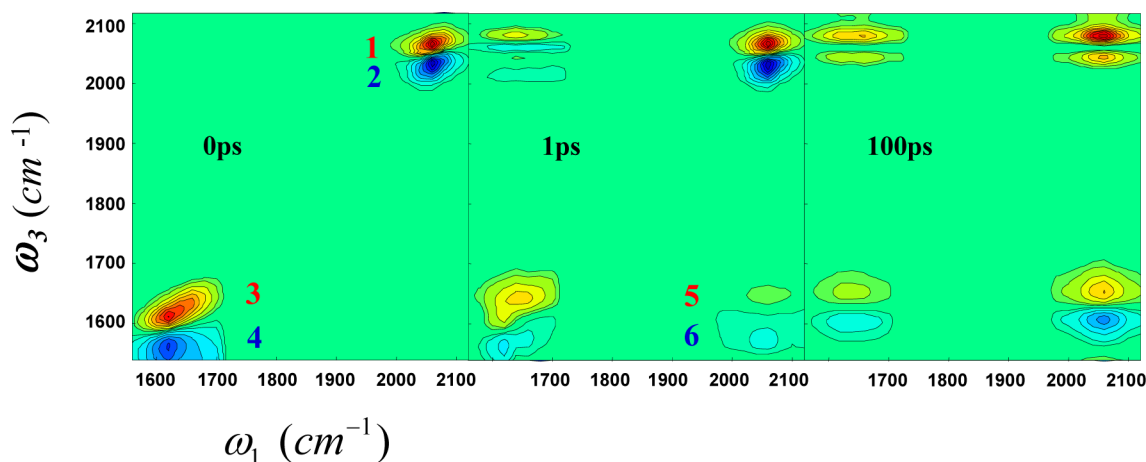


Figure 2. Waiting time dependent 2D IR spectra of the KSCN/H₂O (1/10 molar ratio) solution. The pump power at 2060 cm^{-1} is 7.1 mW. The pump power at 1640 cm^{-1} is 3.3 mW. Intensities of CN peaks are divided by 30 times to clearly display other peaks.

measure the energy transfer from the CN stretching mode of SCN⁻ to the HOH bending mode of water between the anion SCN⁻ and the water molecules. By comparing the energy transfers among these species in the KSCN/H₂O (1/10 molar ratio) solution and the NH₄SCN/H₂O (1/10 molar ratio) solution and other solutions with different ion concentrations, we obtained clear evidence that more than 50% of the SCN⁻ anions in the NH₄SCN/H₂O (1/10 molar ratio) solution have direct contact with the NH₄⁺ cations.

2. EXPERIMENTAL SECTION

The experimental setup has been described elsewhere.^{16,17} Briefly, a ps amplifier and a fs amplifier are synchronized with the same pulse from a Ti-sapphire oscillator generating a pulse centered at $\sim 800 \text{ nm}$ with a bandwidth $\sim 35 \text{ nm}$ and power $\sim 600 \text{ mW}$. The ps amplifier pumps an OPA to produce 0.7–1 ps Mid-IR pulses with a bandwidth $\sim 21 \text{ cm}^{-1}$ ($10\text{--}27 \text{ cm}^{-1}$) in a tunable frequency range from 500 to 4000 cm^{-1} with energy 1–40 $\mu\text{J}/\text{pulse}$ at the repetition rate of 1 kHz. The fs amplifier pumps a fs OPA to produce $\sim 110 \text{ fs}$ Mid-IR pulses with a bandwidth $\sim 200 \text{ cm}^{-1}$ in a tunable frequency range from 500 to 4000 cm^{-1} with energy 1–40 $\mu\text{J}/\text{pulse}$ at 1 kHz. In experiments, the ps IR pulse is the excitation beam. The fs IR pulse is the detection beam which is frequency resolved by a spectrograph yielding the probe axis (ω_3) of a 2D IR spectrum. Scanning the excitational frequency yields the other axis (ω_1) of the spectrum. Two polarizers are inserted into the detection beam path to selectively measure the parallel or perpendicular polarized signal relative to the pump beam. Vibrational lifetimes

are obtained from the rotation-free signal $P_{\text{life}} = P_{\parallel} + 2 \times P_{\perp}$, where $P_{\parallel}$ and $P_{\perp}$ are parallel and perpendicular data, respectively. Rotational relaxation times are acquired from $r = (P_{\parallel} - P_{\perp}) / (P_{\parallel} + 2 \times P_{\perp})$.

D₂O was purchased from C/D/N Isotopes Inc. KSCN, NH₄SCN, and NH₄Br were purchased from Aldrich and used as received. The liquid samples, used for the experimental measurements, were contained in a sample cell composed of two CaF₂ windows separated by a Teflon spacer. The thickness of the spacer was adjusted accordingly to the optical densities. The experimental optical path and apparatus were purged with dry air free of CO₂. All of the measurements were carried out at room temperature (297 K).

The structural and vibrational calculations were carried out as implemented in the Gaussian 09 program suite.¹⁸ The level and basis set used were Becke's 3-parameter hybrid functional combined with the Lee–Yang–Parr correction functional, abbreviated as B3LYP, and 6-311+G(d,p). Both isolated molecules and molecules in solvent (water) with the CPCM model were calculated.

3. RESULTS AND DISCUSSIONS

3.1. Vibrational Energy Dynamics of the KSCN/H₂O (1/10) Solution. 3.1.1. CN to OH Energy Transfer Time is 3.1 ps.

Figure 1 A displays the FTIR spectra of a KSCN/H₂O (1/10 molar ratio) solution and a KSCN/D₂O (1/10 molar ratio) solution. Based on DFT calculations, the peak at 2066 cm^{-1} is assigned to the CN stretching mode of SCN⁻. The peak at 1636 cm^{-1} is assigned to the HOH bending mode of H₂O. In

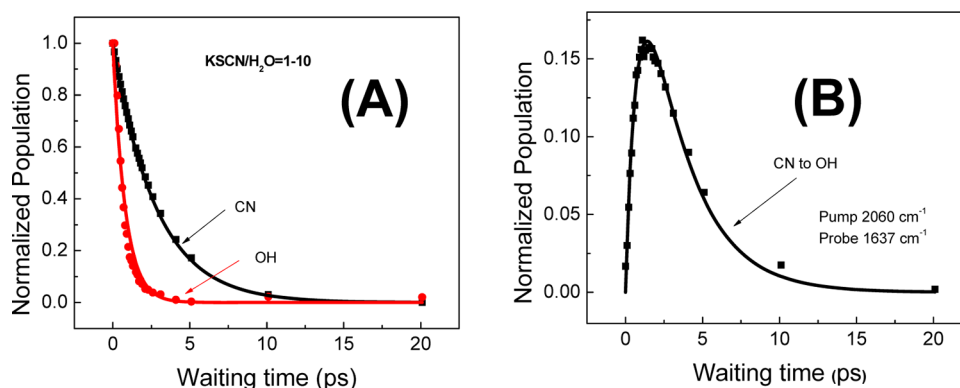


Figure 3. (A) Time dependent populations of the 1st excited states of CN stretch and HOH bending, and (B) the CN to OH energy transfer in the KSCN/H₂O (1/10) solution (pump 2060 cm⁻¹, probe 1637 cm⁻¹). The dots are experimental data and the lines are calculations.

the D₂O solution, the bending mode shifts to a lower frequency 1203 cm⁻¹ because of the deuterium's heavier mass. Figure 1C displays the FTIR spectra of a KSCN/H₂O (1/10 molar ratio) solution, a NH₄SCN/H₂O (1/10 molar ratio) solution, and a NH₄Br/H₂O (1/10 molar ratio) solution. The 1450 cm⁻¹ peak is assigned to the NH₄ bending mode. Peak C (~2060 cm⁻¹) is assigned to a combination band of NH₄⁺ which is composed of the NH₄ bending mode and some other low frequency modes. Peak C' (~2060 cm⁻¹) in Figure 1B is assigned to a combination band of water which is composed of the HOH bending mode and some other low frequency modes. The existences of these two combination bands have profound effects on the energy transfers studied in this work, which will be discussed in the following. Here, the nature of a combination is briefly explained. A combination band results from two or more fundamental vibrations (normal modes) are excited simultaneously because of the anharmonic nature of molecular vibrations.¹⁹ The frequency of a combination band is generally a few percent or less, depending on the combination anharmonicity, smaller than the frequency sum of the fundamentals. The decomposition of the combination band excitation into the excitations of fundamentals can proceed through the dephasing mechanism: the vibrational excitations of the fundamentals are out of phase because of molecular collisions. In room temperature liquids, vibrational dephasings are typically faster than a few ps.^{20,21}

The vibrational frequency differences between D₂O and H₂O have a dramatic effect on the vibrational dynamics of the CN stretch of SCN⁻ dissolved in them. The lifetime of its first vibrational excited state drops from 23 ± 2 ps in the D₂O solution to only 2.8 ± 0.2 ps in the H₂O solution. Data are provided in the Supporting Information. Vibrational energy exchange measurements in Figures 2 and 3 show that 90% (population ratio based on the measured rate constants) of the initial excitation of the CN stretch in the KSCN/H₂O solution is transferred to the HOH bending with a time constant 3.1 ± 0.2 ps. The result suggests that the six times faster relaxation of the excited CN stretch in H₂O than in D₂O is primarily caused by the energy transfer from the CN stretch to the HOH bending mode of H₂O. In the following discussion, the analysis of energy kinetics is presented.

Figure 2 displays the waiting time dependent 2D IR spectra of the KSCN/H₂O (1/10 molar ratio) solution. The peaks in the spectra are very similar to those in the vibrational energy transfer spectra investigated before.^{14,22,23} The peak generation mechanism has been described in our previous publica-

tions.^{14,22,23} Here, only a brief explanation is provided. At time zero, only the diagonal peak pairs show up. The red peak 1 at ($\omega_1 = 2066$ cm⁻¹, $\omega_3 = 2066$ cm⁻¹) is the 0–1 transition of the CN stretch, and the blue peak 2 at ($\omega_1 = 2066$ cm⁻¹, $\omega_3 = 2035$ cm⁻¹) is the 1–2 transition of the CN stretch. The red peak 3 at ($\omega_1 = 1636$ cm⁻¹, $\omega_3 = 1636$ cm⁻¹) is the 0–1 transition of the HOH bending, and the blue peak 4 at ($\omega_1 = 1636$ cm⁻¹, $\omega_3 = 1580$ cm⁻¹) is the 1–2 transition of the HOH bending. With the increase of waiting time to 1 ps, vibrational energy begins to exchange. The energy transfer from the CN stretch down to the HOH bending produces cross peak pairs 5 ($\omega_1 = 2066$ cm⁻¹, $\omega_3 = 1636$ cm⁻¹) and 6 ($\omega_1 = 2066$ cm⁻¹, $\omega_3 = 1580$ cm⁻¹). According to the detailed balance principle, the rate of energy transfer from the HOH bending up to the CN stretch is only 13% ($e^{-(2060-1640)/205} = 0.13$) of that of the energy down-flowing process. The transfer is too slow to be experimentally observed at 1 ps. However, because the vibrational lifetime of HOH bending is only ~0.8 ps, at waiting time 1 ps, some of the HOH bending excitation has relaxed into heat and produced the cross peaks in the frequency range of $\omega_1 = 1636$ cm⁻¹, $\omega_3 = 2030$ – 2090 cm⁻¹. When the waiting time increases to 100 ps, most of the OH and CN vibrational excitations have relaxed into heat because of their short lifetimes. The peaks in the 100 ps spectrum are the results of heat induced absorption (blue) or bleaching (red), as observed in other systems.²³ The heat induced peaks have different frequencies from the normal 0–1 and 1–2 transition frequencies, as shown in Figure 2. The frequency difference allows the pure vibrational energy transfer from CN to OH and vibrational relaxation information to be extracted from the somewhat overlapped signals by removing the heat effect from the overall signals at the CN and OH 0–1 or 1–2 transition frequencies.²³

To quantitatively analyze the energy transfer kinetics from the CN stretch to the HOH bending, the vibrational relaxations of the HOH bending and the CN stretch and the energy transfer between them were simultaneously analyzed with the vibrational energy exchange model previously developed,²² as shown in scheme I:



In the model, the excitations of CN and OH can exchange, and both of them decay with their own vibrational lifetimes ($1/k_{\text{OH}}$ and $1/k_{\text{CN}}$) which were independently measured with some extent of uncertainty. The uncertainty is primarily

because experimentally there is no way to create an exact situation as the measured sample where the pure lifetimes can be exactly measured without involving the energy exchange. Therefore, in the calculation, we allowed the vibrational lifetime $1/k_{\text{CN}}$ of CN to vary by about 50% from the lifetime 23 ps determined in the D_2O solution, because it is not immediately clear what its exact lifetime would be in H_2O without the influence of the HOH bending. The HOH bending lifetime $1/k_{\text{OH}}$ is only allowed to vary by 20% from the determined 0.8 ps in H_2O , because we assume that the very fast relaxation must be mainly caused by intramolecular couplings which should be bigger than the influence of KSCN. The time dependent CN excited (normalized) population $[\text{CN}]$ is the normalized intensity of peak 1. The time dependent OH excited population $[\text{OH}]$ is the normalized intensity of peak 3. The time dependent energy transfer population from CN to OH is the normalized intensity of the cross peak 5. As discussed previously,^{14,22,23} with the proper removal of heat effect, either blue peaks or red peaks can be used to analyze energy transfer kinetics. In the analysis here, that red peaks rather than blue peaks were chosen to analyze the energy transfer kinetics is mainly because the blue cross peak 6 is more severely affected by the heat effect than the red cross peak 5. In the following kinetic analyses for other solutions, the choice of either red or blue peaks is dependent on the heat effect. All data are rotation-free. The energy transfer rate constant ratio $k_{\text{OH} \rightarrow \text{CN}}/k_{\text{CN} \rightarrow \text{OH}} = 0.13$ is determined by the detailed balance principle. Therefore, there is only one unknown parameter, the energy transfer rate constant $k_{\text{CN} \rightarrow \text{OH}}$ in the analysis. Calculations yield $1/k_{\text{CN} \rightarrow \text{OH}} = 3.1 \pm 0.2$ ps with parameters $1/k_{\text{OH}} = 0.8$ ps and $1/k_{\text{CN}} = 30$ ps. The calculation results fit the experimental data very well, as shown in Figure 3. Different from our previous experiments^{14,15,22,23} where vibrational lifetimes and energy transfer times are significantly slower than the instrumental response time 0.7–1 ps, in the experiments presented here, the lifetime of HOH bending mode is close to the instrumental response time. Therefore, the instrumental response function is needed to deconvolute the data. The deconvolution detail and the discussion about the vibrational lifetimes of HOH bending mode^{24–26} are provided in the Supporting Information.

3.1.2. Combination Band C' is Probably Involved in the CN/OH Energy Transfer. As discussed above, in the KSCN/ H_2O (1/10 molar ratio) solution, the energy transfer time constant from the CN stretch to the HOH bending is $1/k_{\text{CN} \rightarrow \text{OH}} = 3.1 \pm 0.2$ ps. The apparent vibrational lifetime of the CN stretch in this solution is determined to be 2.8 ± 0.2 ps, indicating that $\sim 90\%$ $[(1/3.1)/(1/2.8)]$ of the initial CN excitation transfers to the HOH bending of the water molecule. Compared to this relatively short lifetime in H_2O , its lifetime, 23 ± 2 ps, in D_2O is much longer. If the detected $1/k_{\text{CN} \rightarrow \text{OH}} = 3.1 \pm 0.2$ ps in H_2O results from the direct transfer from CN to OH without going through a bridge state, the outcome would indicate that the frequency shift of hydroxyl bending from 1636 (OH) to 1203 cm^{-1} (OD) significantly slows down the energy transfer between the SCN^- anions and the water molecules, if the dipole/dipole interaction mechanism dominates the energy transfers.²⁷ However, H_2O has a combination band C' at ~ 2100 cm^{-1} as shown in Figure 1B. It is possible that the CN excitation can first quasi-resonantly transfer to the combination band C' through the dipole/dipole interaction mechanism which seems to hold for all intermolecular vibrational energy transfers we have investigated so far.^{14,15} Then the excitation can be transferred intramolecularly from this combination band

to the HOH bending through mechanisms other than the dipole/dipole interaction, e.g. through bond or mechanical coupling or dephasing. To further address this issue, the vibrational energy transfer equation (eq 1) derived from our previous experiments^{14,23} and the dipole/dipole interaction equation (eq 2) were used:

$$k_{\text{DA}} = \frac{1}{1 + e^{-\Delta\omega_{\text{DA}}/RT}} \langle\beta\rangle^2 \frac{\frac{1}{\tau_c}}{\left(\frac{1}{\tau_c}\right)^2 + (\Delta\omega_{\text{DA}})^2} \quad (1)$$

where k_{DA} is the energy transfer rate constant from the donor (D) to the acceptor (A). $\Delta\omega_{\text{DA}} = \omega_{\text{D}} - \omega_{\text{A}}$ is the frequency difference between the donor and the acceptor, R is the gas constant, T is the temperature, $\langle\beta\rangle$ is the average coupling constant between D and A, and τ_c is the coupling fluctuation time. For all the room temperature liquids we studied so far, τ_c was found to be 2.0 ± 0.1 ps. This is at the same time scale as that of solvent molecules reorganizing their configurations, corresponding to the molecular binding enthalpy ~ 0.6 kcal/mol which is the same as the thermal energy at room temperature.²⁸ $(1/\tau_c)^2$ is a value in the energy or frequency unit corresponding to each τ_c . $(1/\tau_c)^2 = 16.7$ cm^{-1} for $\tau_c = 2$ ps. The dipole/dipole interaction equation is

$$\begin{aligned} \langle\beta\rangle &= \frac{1}{4\pi\epsilon_0 n^2} \left[\frac{\boldsymbol{\mu}_{\text{D}} \cdot \boldsymbol{\mu}_{\text{A}}}{r_{\text{DA}}^3} - 3 \frac{(\boldsymbol{\mu}_{\text{D}} \cdot \mathbf{r}_{\text{DA}})(\boldsymbol{\mu}_{\text{A}} \cdot \mathbf{r}_{\text{DA}})}{r_{\text{DA}}^5} \right] \\ &= \frac{1}{4\pi\epsilon_0 n^2} \frac{\mu_{\text{D}} \mu_{\text{A}} \kappa}{r_{\text{DA}}^3} \end{aligned} \quad (2)$$

where ϵ_0 is the vacuum permittivity, n is the local refractive index of the media, $\kappa = \cos \theta_{\text{DA}} - 3 \cos \theta_{\text{D}} \cos \theta_{\text{A}}$, θ_{AD} is the angle between the two transition dipole moments, and θ_{A} and θ_{D} are the angles between each transition moment and the vector connecting them. $\boldsymbol{\mu}_{\text{D}}$ and $\boldsymbol{\mu}_{\text{A}}$ are the transition dipole moments of donor and acceptor, respectively. r_{DA} is the distance between the donor and acceptor.

If we assume that the refractive indexes, the couplings between the CN stretch and the OH and OD bendings, and the coupling fluctuation times are all the same in the D_2O and H_2O solutions, the energy transfer time constant from the CN stretch to the OD bending would be ~ 13 ps based on the observed $1/k_{\text{CN} \rightarrow \text{OH}} = 3.1 \pm 0.2$ ps, and eq 1 which had been examined to work well for energy transfer times from 6 to 120 ps with isotope-labeled experiments.¹⁴ The transition dipole moment square of DOD bending is about 15% smaller than that of HOH bending as measured with FTIR, resulting in a 15% smaller CN/OD vibrational coupling. Counting for this difference, the energy transfer time constant from the CN stretch to the OD bending would be ~ 15 ps. Because the CN vibrational lifetime in D_2O is 23 ps, it is unlikely for $1/k_{\text{CN} \rightarrow \text{OD}}$ to be faster than 23 ps. The estimated 15 ps is too fast. This can be from two reasons: one is that some assumptions in the estimation can be invalid, and the other, in H_2O , the CN excitation can quickly transfer (because of quasi-resonance) to the combination band at ~ 2100 cm^{-1} and then transfer to the HOH bending through a different mechanism other than the direct energy transfer from CN to OH. Based on eqs 1 and 2, the transfer rate from CN to the combination band C' (resonant) is about 30 times faster than that directly from the CN stretch to the HOH bending, assuming that the only differences between these two transfers are the transition dipole

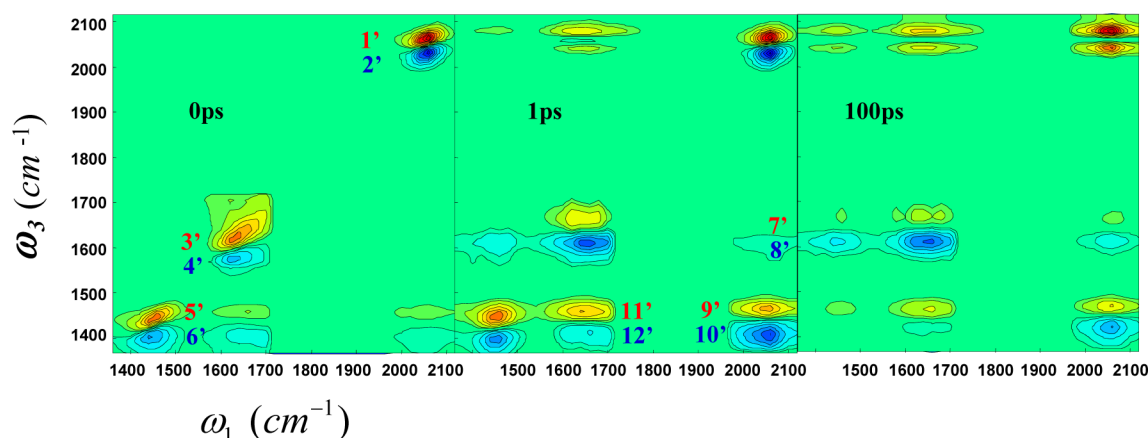


Figure 4. Waiting time dependent 2D IR spectra of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution. The pump power at 2060 cm^{-1} is 7.3 mW. The pump power at 1640 cm^{-1} is 3.3 mW, and the pump power at 1450 cm^{-1} is 1.7 mW. Intensities of the CN peaks are divided by 30 times to clearly display other peaks.

moments ($(\mu_{\text{OH}}/\mu_{\text{com}})^2 = 10$) and the energy mismatches (0 and 429 cm^{-1}). D_2O lacks such a bridge mechanism because it does not have a combination band of which the frequency overlaps with that of the CN stretch. Therefore, the CN stretch relaxes much slower in D_2O . If we assume that the CN lifetime of 23 ps in D_2O is mainly contributed by the relaxation to the OD bending, the direct CN/OH transfer time in the H_2O solution would be 5.5 ps (the fast limit) according to eq 1. Estimated from the analysis, the transfer rate through the bridge mechanism is about 7.2 ps [$1/3.1 = 1/5.5 + 1/7.2$]. In pure H_2O , the transfer of combination band C' excitation to the HOH bending was not observed, probably because the transition dipole moment of combination C' is so weak that the energy transfer peak is too small to be observed. Data are shown in the Supporting Information, Figure S5.

In summary, in the $\text{KSCN}/\text{H}_2\text{O}$ (1/10 molar ratio) solution, $\sim 90\%$ of the CN stretch first vibrational excited state excitation of the SCN^- anions transfers to the HOH bending mode of the solvent molecules with a time constant ~ 3.1 ps. In addition to the direct CN/OH energy transfer mechanism, it is also conceivable that the transfer can be directed through a bridge mechanism where the H_2O combination band at $\sim 2100\text{ cm}^{-1}$ functions as a bridge state between the CN stretch and the HOH bending.

3.2. Vibrational Energy Dynamics of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) Solution. Different from the $\text{KSCN}/\text{H}_2\text{O}$ (1/10) solution where only H_2O molecules are the intermolecular vibrational energy acceptors, in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution NH_4^+ can provide additional energy acceptors for the excited CN stretch from SCN^- . Both its combination band at $\sim 2060\text{ cm}^{-1}$ and NH bending at 1460 cm^{-1} (see FTIR spectra in Figure 1C) are the two most obvious energy accepting modes. If the molecules in the solutions are randomly distributed and can fast switch their locations, the vibrational relaxation of the CN stretch would be expected to be faster in the NH_4SCN solution than in the KSCN solution because it has more energy acceptors. In fact, experimentally the vibrational relaxation (3.1 ps) of CN stretch in the NH_4SCN solution is actually a little slower than that (2.8 ps) in the KSCN solution. Vibrational energy exchange measurements show that in the NH_4SCN solution, the energy transfer from the CN stretch to the HOH bending of H_2O slow down to 6.3 ps from 3.1 ps in the KSCN solution, and the energy transfer

from the CN stretch to the NH bending of NH_4^+ takes a similar time of 7.0 ps. In other words, in the NH_4SCN solution, only 49% of the CN initial excitation is transferred to the HOH bending instead of $\sim 90\%$ in the KSCN solution. 44% of the CN excitation is transferred to the NH bending, and the remaining 7% is transferred to other intra- and intermolecular acceptors.

Figure 4 displays the 2D IR spectra of the $\text{KSCN}/\text{H}_2\text{O}$ (1/10) solution. Similar to Figure 3, the diagonal peak pairs 1' and 2', 3' and 4', 5' and 6' belongs to the 0–1 and 1–2 transitions of the CN stretch, the HOH bending, and the NH bending, respectively. Cross peak pairs 7' and 8' are from the vibrational energy transfer from CN to OH, and the heat effect inducing HOH bending absorption change. The excitation frequency at 2066 cm^{-1} (Figure 4, 1 ps) shows that the energy source of heat is from the initial CN excitation of which one portion is remained in CN and one portion is transferred to OH. The relaxations of both portions produce the heat effect at frequencies around peak 7' and 8'. The energy transfer and the heat effect produce peaks at slightly different frequencies. Similarly, cross peak pairs 9' and 10' are from the vibrational coupling between CN and NH and between combination band C and NH, the vibrational energy transfer from CN to NH and from C to NH, and the heat effect inducing NH bending absorption change. The contribution from C to NH can be manifested by the broader excitation frequency ω_1 of the cross peaks 9' and 10' than that of the corresponding diagonal peaks 1' and 2' in Figure 4. This contribution can also be straightforwardly seen from the pump/probe data on $\text{NH}_4\text{Br}/\text{H}_2\text{O}$ (1/10) solution provided in Figure S5(F). Cross peak pairs 11' and 12' are from the vibrational coupling between NH and OH, the vibrational energy transfer from OH to NH, and the heat effect inducing NH bending absorption change. The energy transfer from C to NH produces peaks at the same frequencies as the transfer from CN to NH. In the CN/NH and CN/OH energy transfer kinetic analysis, we removed the possible contributions of C to NH and OH transfers by subtracting the signal of the $\text{NH}_4\text{Br}/\text{H}_2\text{O}$ (1/10) solution from that of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ solution of the same concentration and the same NH bending optical density.

In the NH_4SCN solution, two intermolecular acceptors, the HOH bending mode of H_2O and the NH bending mode of NH_4^+ , are competing for the CN excitation. In addition, the

energy of OH and NH can also exchange. The vibrational excitations of these modes also decay with their own lifetimes. These dynamic processes are coupled to each other. It would be very complicated to solve the completely coupled kinetic equations. However, the different time scales of different processes allow us to decouple some of them: (1) the lifetime of HOH bending is ~ 0.8 ps, and the energy transfer time from OH to NH is 4 ps (see the Supporting Information). Therefore, only $\sim 12\%$ of the HOH bending excitation will be transferred to the NH bending. (2) because the frequency of NH bending is 186 cm^{-1} lower than that of the HOH bending, the energy transfer rate from NH up to OH is only $\sim 40\%$ of the OH/NH down flowing rate, ~ 10 ps, which is much slower than the lifetime of either the HOH bending (0.8 ± 0.2 ps) or the NH bending (1.3 ± 0.2 ps). In other words, only a small portion of the OH or NH bending vibrational excitation can exchange between them. Therefore, omitting the energy exchange between the OH and NH bendings in processing the energy transfers from CN to OH and NH will not cause a big error. The kinetic equations are then simplified into two sets of independent equations: one is from CN to NH, and the other is from CN to OH. Each set is similar to that for the CN/OH transfer in the KSCN/H₂O solution.

Solving the kinetic equations yields $1/k'_{\text{CN} \rightarrow \text{OH}} = 6.3 \pm 0.5$ ps with parameters $1/k'_{\text{OH}} = 0.8$ ps, $1/k'_{\text{CN}} = 5.5$ ps, and $1/k'_{\text{CN} \rightarrow \text{NH}} = 7.0 \pm 0.5$ ps with parameters $1/k_{\text{NH}} = 1.3 \pm 0.2$ ps and $1/k''_{\text{CN}} = 5.2$ ps. Different $1/k_{\text{CN}}$ values were used because the relaxation channels of CN include three parts: (1) to NH, (2) to OH, and (3) to other modes (assumed to be about 30 ps). In calculating either the CN/NH or the CN/OH energy transfer rate constant, $1/k_{\text{CN}}$ is the sum of two contributions (to other modes + to OH or to NH). Calculations and experimental results are shown in Figure 5. The results indicate that $\sim 49\%$ of the CN excitation flows to the HOH bending, and $\sim 44\%$ flows to the NH bending. These results can be immediately observed by directly comparing the normalized cross peak intensities in Figure 4B. The CN/OH cross peak of

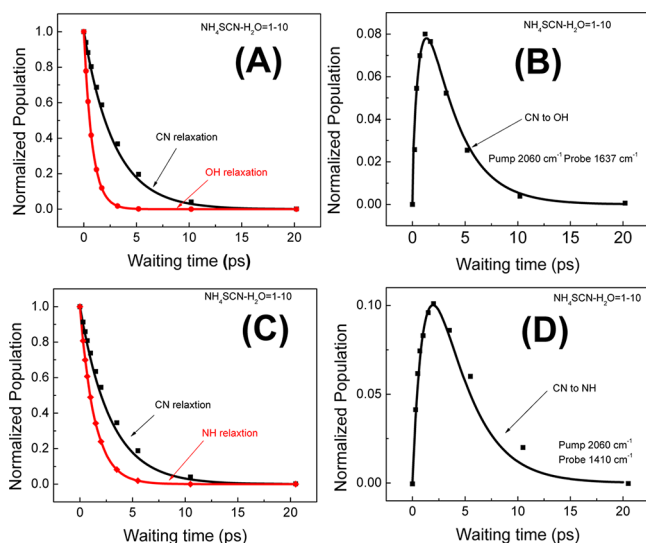


Figure 5. (A) Time dependent populations of the 1st excited states of CN stretch and HOH bending, (B) the CN to OH energy transfer (pump 2060 cm^{-1} , probe 1637 cm^{-1}), (C) the 1st excited states of CN stretch and NH bending, and (D) the CN to NH energy transfer in the NH₄SCN/H₂O (1/10) solution (pump 2060 cm^{-1} , probe 1410 cm^{-1}). Dots are data, and lines are calculations.

the KSCN/H₂O solution (Figure 2B) is about 100% larger than that of the CN/OH cross peak of the NH₄SCN solution (Figure 4B). The simple inspection on the peak intensity is consistent with the quantitative analysis that about 100% more CN energy is transferred to the HOH bending in the KSCN solution than in the NH₄SCN solution.

3.3. NH₄⁺ Competing with H₂O to Bind to SCN⁻. The above energy transfer kinetic measurements show that the vibrational energy transfer from the CN stretch of SCN⁻ to the HOH bending of H₂O in the KSCN/H₂O (1/10) solution is very efficient. $\sim 90\%$ of the CN excitation can be transferred to OH with a time constant 3.1 ps. However, in the NH₄SCN/H₂O (1/10) solution, the CN/OH energy transfer efficiency drops for about one-half to $\sim 49\%$ with a more than 100% slower time constant 6.3 ps. The rest 41% which goes to OH in the KSCN solution now flows into the NH bending of the NH₄⁺. The most obvious explanation is that, NH₄⁺ directly competes with H₂O for binding to SCN⁻. H₂O molecules of about $51\% \pm 12\%$ $[(1/3.1) - (1/6.3)/(1/3.1)]$ of the SCN⁻/H₂O binding sites in the KSCN solution are replaced by the NH₄⁺ cations in the NH₄SCN solution. Only $49\% \pm 12\%$ of the SCN⁻ anions remain bound to H₂O so that the CN/OH energy transfer time constant drops from 3.1 ps to 6.3 ps. The other $51 \pm 12\%$ SCN⁻ anions bind to the NH₄⁺ cations, forming the CN/NH energy transfer pathway with a time constant 7.0 ps. However, before this conclusion can be finally reached, a few concerns need to be addressed: (1) With the fact that in the 1/10 KSCN/H₂O solution, K⁺ also binds to SCN⁻, does this binding affect the CN/OH energy transfer? (2) Is it possible that the slowed down CN/OH energy transfer rate in the NH₄SCN solution is caused by the weakening of the interaction between SCN⁻ and H₂O by the H₂O/NH₄⁺ interaction rather than the competition between NH₄⁺ and H₂O for binding to SCN⁻? (3) Is it possible that the slowed down CN/OH energy transfer rate in the NH₄SCN solution is caused by the “forced contact”, the statistical chance based on the number ratio for NH₄⁺ cations to replace some H₂O molecules to bind to SCN⁻? (4) Is it possible that the transition dipole moment of either the NH bending or C is much larger than that of the OH bending or C' where the energy prefers to transfer from SCN⁻ to NH₄⁺ even if they are separated by a water molecule?

In the KSCN/H₂O (1/10) solution, about 67% of the anions form clusters.¹⁵ The vibrational lifetime of CN stretch is 2.8 ± 0.2 ps. In a 0.5 M KSCN solution (KSCN/H₂O = 1/100) where less than 20% of the anions form clusters, the vibrational lifetime of CN stretch is 2.5 ± 0.2 ps. In a 0.05 M KSCN H₂O solution (KSCN/H₂O = 1/1000), very few anions form clusters (the cluster concentration is too low for our method to detect) because of the low ion concentration. The vibrational lifetime of CN slightly decreases to 2.4 ± 0.2 ps (see the Supporting Information). The results indicate that the ion clustering does have a small effect on the CN/OH energy transfer. The effect can come from two possible reasons. One is that the ion clustering can change the environment of SCN⁻ anions so that the intramolecular relaxation of CN stretch can be different. The other reason is that although the cation K⁺ cannot accept vibrational energy from the CN excitation, its rotational time ~ 4.2 ps (in the 1/10 KSCN/H₂O solution) is a little longer than the CN/OH transfer time. This can probably force the clustered SCN⁻ anions to spend extra time to adjust positions in order to transfer energy to water. Nonetheless, the effect of ion clustering is small. The CN/OH energy transfer time is

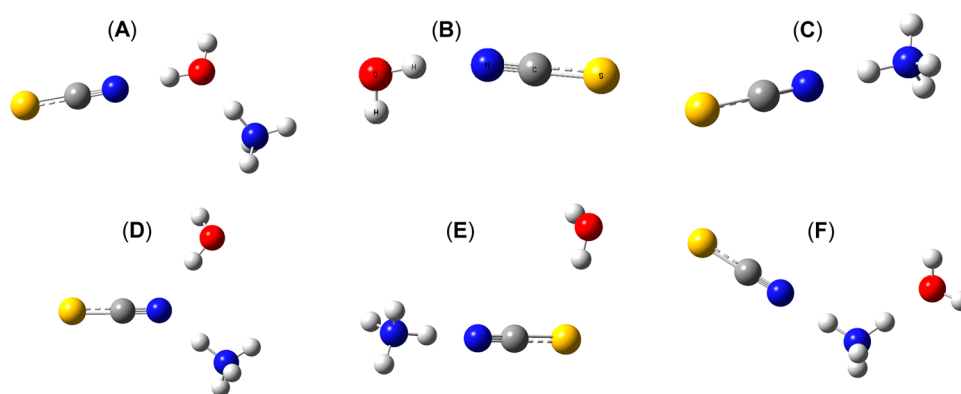


Figure 6. (A) Calculated SCN^- – H_2O – NH_4^+ trimer structure with the CPCM water solvent. (B) Calculated most stable $\text{SCN}^-/\text{H}_2\text{O}$ structure with the CPCM water solvent. (C) Calculated most stable $\text{SCN}^-/\text{NH}_4^+$ structure with the CPCM water solvent. (D) Calculated trimer conformation with NH_4^+ directly bound to the CN group, $\Delta E = -13.9$ kcal/mol. (E) Calculated trimer conformation with NH_4^+ directly bound to the CN group, $\Delta E = -13.4$ kcal/mol. (F) Calculated trimer conformation with NH_4^+ directly bound to the CN group, $\Delta E = -16.3$ kcal/mol.

changed for at most 14% from the 0.05 M solution $1/k_{\text{CN} \rightarrow \text{OH}} = 2.6$ ps, estimated from the measured CN apparent lifetime 2.4 ps and $1/k_{\text{CN}} = 30$ ps to the 1/10 solution $1/k_{\text{CN} \rightarrow \text{OH}} = 3.1$ ps.

Issues (2) and (4) are correlated to each other. The central question is whether the NH_4^+ cation can overpower H_2O for accepting the CN excitation of SCN^- even when NH_4^+ and SCN^- are separated by at least one water molecule. Here we analyze two extreme conditions. One is that the CN/OH or CN/NH transfers are dominated by the bridge mechanism through the fast CN/C' or CN/C transfers, and the other is that the direct transfer mechanism dominates the CN/OH or CN/NH transfers. From 1D and 2D IR measurements, the transition dipole moment square ratio of C (the combination band of NH_4^+ at ~ 2060 cm^{-1}) to C' (the combination band of H_2O at ~ 2100 cm^{-1}) is $\mu_{\text{C}'}^2/\mu_{\text{C}}^2 \cong 3.3$. Because the spectra of both C and C' severely overlap with that of the CN stretch, we consider both CN/C and CN/C' transfers are resonant. From DFT calculations, the distance between CN and C' of a SCN^- – H_2O – NH_4^+ trimer (Figure 6A) is ~ 3.3 Å (from the CN bond center to O of H_2O), and the CN/C distance is about 5.1 Å (from the CN bond center to N of NH_4^+). If the other two factors in eq 2, the local refractive index and the cross angle of transition dipole moments which are experimentally difficult to access, are assumed to be the same for both C and C', the energy transfer rate ratio between the CN/C' transfer and the CN/C transfer is $k_{\text{CN} \rightarrow \text{C}'} / k_{\text{CN} \rightarrow \text{C}} = 4$, according to eqs 1 and 2. With a $\text{NH}_4^+/\text{H}_2\text{O}$ molar ratio of 1/10 in the solution, statistically, the chance for an NH_4^+ to stay as shown in Figure 6A, is only 1/10. Therefore, the estimated ratio $k_{\text{CN} \rightarrow \text{C}'} / k_{\text{CN} \rightarrow \text{C}}$ should be 40 instead of 4. The estimation suggests that the chance for the NH_4^+ to out compete H_2O for the CN excitation from SCN^- if both the SCN^- and NH_4^+ are separated by a H_2O molecule (like that in the SCN^- – H_2O – NH_4^+ trimer form, as shown in Figure 6A) is minute for the bridge mechanism. In addition, the resonant energy transfer between C' and C is too slow to be experimentally observed, compared to the C/NH energy transfer. Simultaneously exciting C and C' at 2066 cm^{-1} in the $\text{NH}_4\text{Br}/\text{H}_2\text{O}$ (1/10 molar ratio) solution does not produce any evidence of energy transfer to the HOH bending. Absorption at ~ 1580 cm^{-1} (the most direct evidence of energy transferred to OH) which corresponds to the OH 1–2 transition is not observed, similar to what happens for the pure H_2O sample. On the contrary, the excitation clearly produces absorption at ~ 1410 cm^{-1} which corresponds to the

NH 1–2 transition, indicating energy has transferred to the NH bending. The results imply that the C and C' energy exchange is very slow. Otherwise, we would have been able to observe the energy transfer to OH. All detail data are shown in the Supporting Information, Figure S5.

If the CN/OH and CN/NH direct transfer mechanism dominates, we can directly compare the abilities of OH and NH as the energy acceptor for the CN excitation based on eqs 1 and 2 to estimate the possibility of energy transfer from SCN^- to NH_4^+ separated by at least one H_2O molecule. From both the 1D and 2D IR measurements, the ratio of the transition dipole moment square of NH bending over that of HOH bending was determined to be about 5.5. The CN/NH energy mismatch is 604 cm^{-1} , larger than 428 cm^{-1} between CN and OH. According to DFT calculations of the $\text{SCN}^-/\text{H}_2\text{O}/\text{NH}_4^+$ trimer, the orientation factor between CN and OH is 0.53, and that between CN and NH is 0.73. The CN/OH distance is 3.3 Å, and the CN/NH distance is 5.1 Å. Based on these parameters and eqs 1 and 2, the CN/OH and CN/NH energy transfer rate ratio is $(k_{\text{CN} \rightarrow \text{OH}}/k_{\text{CN} \rightarrow \text{NH}}) = 2.7$. Again, because the $\text{NH}_4^+/\text{H}_2\text{O}$ ratio is 1/10, the actual rate ratio would be 27 rather than 2.7. The estimation therefore suggests that it is not likely for NH_4^+ to accept energy from CN more efficiently than the H_2O molecule sitting between it and SCN^- . As measured (in Supporting Information), the energy transfer time from HOH bending to NH bending is ~ 4.0 ps, much slower than the OH lifetime 0.8 ps. It is therefore not likely that the more than 100% slowed down CN/OH transfer in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (compared to that in the 0.05 M solution) is caused by the fast OH/NH energy transfer.

In summary, the above analysis shows that it is not likely for NH_4^+ to block energy transfer from SCN^- to H_2O without forming $\text{SCN}^-/\text{NH}_4^+$ direct contact. The “forced contact” because of the high concentration is not a likely reason either. In the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution, the NH/OH ratio is 1/5. If the “forced contact” is the reason, the CN/OH transfer rate would only slow down for only $16\% \pm 2\%$ from 2.6 ps in the 0.05 M solution to 3.1 ps rather than 6.3 ps observed in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution.

3.4. $\text{SCN}^-/\text{NH}_4^+$ Binding Affinity Relative to $\text{SCN}^-/\text{H}_2\text{O}$.

If we assume that the 2.4 ps apparent lifetime of the CN stretch in the 0.05 M KSCN solution is contributed by two parts. One is the CN/OH energy transfer pathway with a time constant 2.6 ps, and the other is the sum of all other pathways with a

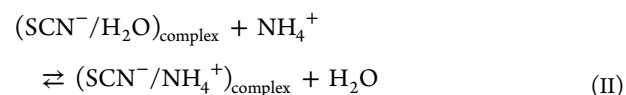
time constant 30 ps which was measured from the KSCN 1/10 aqueous solutions. Because most of the SCN^- anions are surrounded by water molecules in the 0.05 M solution, and the slowdown of CN/OH energy transfer in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution is caused by the competing binding of NH_4^+ to SCN^- , the $\text{SCN}^-/\text{NH}_4^+$ binding affinity relative to that of $\text{SCN}^-/\text{H}_2\text{O}$ can be obtained by comparing the CN/OH energy transfer rate constants in the 0.05 M KSCN solution and the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution. Based on the CN/OH energy transfer time constants 2.6 ps and 6.3 ps, and the $\text{H}_2\text{O}/\text{NH}_4^+$ population ratio 10/1, the ability of NH_4^+ bound to SCN^- is calculated to be about 14 times $\{[(1/2.6) - (1/6.3)]/(1/6.3) \times 10 = 14\}$ of that of water. In other words, in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution, water molecules of $\sim 59\%$ of the $\text{SCN}^-/\text{H}_2\text{O}$ binding sites that would exist in the 0.05 M solution are replaced by NH_4^+ . Here we assume that replacement of H_2O by NH_4^+ is one for one. The ratio is much higher than the 16% of $\text{NH}_4^+/\text{SCN}^-$ binding because of the “forced contact”. The result indicates that the cation/anion binding in the aqueous solutions is mainly because of the chemical nature of the solutions rather than the simple “forced contact” because of the high concentration.

In our previous work,^{14,15} we found that 67% of the SCN^- anions are associated with other anions in a KSCN/ D_2O (1/10) solution through measuring the nonresonant vibrational energy transfer among the SCN^- and $\text{S}^{13}\text{C}^{15}\text{N}^-$ anions. In this work, 59% of the NH_4^+ cations were found to directly bind to the SCN^- anions in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution. The two numbers are very close. However, in the two experiments, the criteria of “association” or “binding” are different because of different experimental observables. In this work, “binding” represents the direct interaction between NH_4^+ and SCN^- which can effectively block the $\text{H}_2\text{O}/\text{SCN}^-$ binding. According to DFT calculations with the CPCM water solvent, one H_2O or NH_4^+ can form a very strong H-bond with a SCN^- anion ($\Delta E_{\text{SCN}^-/\text{H}_2\text{O}} = -5.4$ kcal/mol and $\Delta E_{\text{SCN}^-/\text{NH}_4^+} = -10.7$ kcal/mol), as shown in Figure 6B,C. We expect that the most efficient CN/OH or CN/NH energy transfer pathway would possibly go through similar structures as in Figure 6B,C because they have the shortest donor/acceptor distances, compared to other less stable conformations. When one H_2O , one NH_4^+ , and one SCN^- form a trimer with NH_4^+ directly binding to the CN bond, calculations give three stable conformations, displayed in Figure 6D–F. In these conformations, E, the least stable conformation, and F, the most stable one, energy from CN probably cannot efficiently transfer to H_2O because of the much larger CN/OH distances, compared to that of the conformation in Figure 6B. In the conformation shown in Figure 6D, energy should be able to transfer from CN to OH because of the relative short distance. However, it is 2.4 kcal less stable than the most stable conformation in Figure 6F. At room temperature, according to the Boltzmann distribution, the energy difference indicates that conformation F will dominate (>90%). In the experiments presented in this work, what we observed is the loss of effective CN/OH energy transfer pathways, and the creation of CN/NH energy transfer pathways. Structures like conformation F are probably those producing such experimental observables. Therefore, “binding” in this work refers to the direct $\text{SCN}^-/\text{NH}_4^+$ interaction probably similar to conformation F.

In our previous work,^{15,23} the “associated” ions were defined as anions which could produce experimentally detectable

vibrational energy transfer signal at the time scale of ~ 100 ps among the thiocyanate anions. Different from $\text{SCN}^-/\text{H}_2\text{O}$ or $\text{SCN}^-/\text{NH}_4^+$ where the binding sites for the H-bonds are relatively well-defined, there are no obvious binding sites for the thiocyanate anions to bind to each other. Therefore, we expect that only if two thiocyanate anions are not completely separated by one or more water molecules, in other words, some parts of the two anions have direct contact, they should be able to exchange energy within the experimentally detectable time scale because the long time scale (~ 100 ps) allows larger variations of the anion/anion distances. The definition can have many more possible conformations compared to the “binding” definition in this work. The previous works was to measure the anion/anion association, whereas this work is to measure cation/anion binding. In addition, NH_4^+ is not necessarily the same as K^+ . The results from these two different systems might not be quantitatively comparable. Nonetheless, both pieces of work point to the same general conclusion: in concentrated strong electrolyte aqueous solutions, ions tend to associate because of the detailed chemistry of the solutions, not the simple numerical statistical “forced contact”.

3.5. Concentration Dependent Relative $\text{NH}_4^+/\text{SCN}^-$ Binding Affinity. If we assume that the replacements of anion-bound H_2O molecules are by the same amount of NH_4^+ cations, the chemical equilibrium in the system for one to one replacement can be simply written as



Its equilibrium constant, $K = [\text{H}_2\text{O}][(\text{SCN}^-/\text{NH}_4^+)_{\text{complex}}]/[\text{NH}_4^+][(\text{SCN}^-/\text{H}_2\text{O})_{\text{complex}}]$, is defined as the relative $\text{NH}_4^+/\text{SCN}^-$ binding affinity. This assumption of one to one replacement can be tested by the concentration dependent energy transfer measurements. Two more samples of different ion concentrations with $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/5$ and $1/25$ (molar ratio) were tested. Data are shown in the Supporting Information.

As shown in Table 1, experiments show that in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/5$ solution, the CN/NH energy transfer

Table 1. Energy Transfer Time Constants and Relative $\text{NH}_4^+/\text{SCN}^-$ Binding Affinities in NH_4SCN Aqueous Solutions of Different Concentrations

sample	CN/NH energy transfer time constant $1/k_{\text{CN} \rightarrow \text{NH}}$ (ps)	CN/OH energy transfer time constant $1/k_{\text{CN} \rightarrow \text{OH}}$ (ps)	the relative $\text{NH}_4^+/\text{SCN}^-$ binding affinity
$\text{NH}_4\text{SCN}-\text{H}_2\text{O} = 1-5$	3.7 ± 0.4	16 ± 3	26 ± 5
$\text{NH}_4\text{SCN}-\text{H}_2\text{O} = 1-10$	7.0 ± 0.5	6.3 ± 0.5	14 ± 3
$\text{NH}_4\text{SCN}-\text{H}_2\text{O} = 1-25$	12 ± 2	4.6 ± 0.4	19 ± 4

time constant is $1/k_{\text{CN} \rightarrow \text{NH}} = 3.7$ ps, and the CN/OH energy transfer time constant is $1/k_{\text{CN} \rightarrow \text{OH}} = 16$ ps. In the $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/25$ solution, the CN/NH energy transfer time constant is $1/k_{\text{CN} \rightarrow \text{NH}} = 12$ ps, and the CN/OH energy transfer time constant is $1/k_{\text{CN} \rightarrow \text{OH}} = 4.6$ ps. The CN/NH and CN/OH energy transfer time constants can be simultaneously used to test the chemical equilibrium equation. Based on the equilibrium equation in scheme II, the CN/OH energy transfer time constant $1/k_{\text{CN} \rightarrow \text{OH}} = 16$ ps in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/5$ solution yields the relative $\text{NH}_4^+/\text{SCN}^-$ binding affinity $K = 26$

± 5 . The CN/OH energy transfer time constant of $1/k_{\text{CN} \rightarrow \text{OH}} = 4.6$ ps in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/25$ solution yields the relative $\text{NH}_4^+/\text{SCN}^-$ binding affinity $K = 19 \pm 4$. $K = 26 \pm 5$ in the $1/5$ solution is a little bigger than those in the more dilute solutions. The CN/NH energy transfer time constants can also be used to derive the binding affinity. If we take the central $K = 19$ as determined, the CN/NH energy transfer time constant can be estimated to $1/k_{\text{CN} \rightarrow \text{NH}} = 4.8 \pm 0.4$ ps for a solution where SCN^- exclusively binds to NH_4^+ from the $1/10$ and $1/25$ $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ solutions. In the $1/25$ solution, the CN/NH energy transfer time constant $1/k_{\text{CN} \rightarrow \text{NH}} = 12$ ps yields the binding affinity $K = (1/12)/(1/4.8) \times 25/(1 - (1/12)/(1/4.8)) \times 1 = 17$. In the $1/10$ solution, the CN/NH energy transfer time constant $1/k_{\text{CN} \rightarrow \text{NH}} = 7.0$ ps yields the binding affinity $K = (1/7.0)/(1/4.8) \times 10/(1 - (1/7.0)/(1/4.8)) \times 1 = 22$. These two affinity values in the $1/10$ and $1/25$ solutions are consistent with the results from the CN/OH energy transfer measurements. However, in the $1/5$ solution, the CN/NH energy transfer time constant $1/k_{\text{CN} \rightarrow \text{NH}} = 3.7 \pm 0.4$ ps is faster than the derived $1/k_{\text{CN} \rightarrow \text{NH}} = 4.8 \pm 0.4$ ps for the 100% $\text{SCN}^-/\text{NH}_4^+$ binding based on $K = 19$. This is surprising. The measured CN/NH energy transfer time constant implies more than 100% $\text{SCN}^-/\text{NH}_4^+$ binding if the $\text{SCN}^-/\text{NH}_4^+$ binding structure remains the same in the $1/10$ and $1/5$ solutions. This is simply impossible. The very likely reason is that the $\text{SCN}^-/\text{NH}_4^+$ binding structure has changed in the $1/5$ solution, compared to those in the $1/10$ and $1/25$ solution. Similar to the KSCN aqueous solutions,¹⁵ in the $1/5$ NH_4SCN solution, the resonant energy transfer among the anions is fast, with a time constant 3–4 ps, indicating significant ion clustering. In the $1/25$ and $1/10$ NH_4SCN solutions, the resonant energy transfer rates among the anions are slower than that in the $1/5$ solution, indicating fewer and smaller ion clusters in these two dilute solutions. It is conceivable that ion clustering can modify the cation/anion complex structures in the solutions because the local environments of the cation/anion complexes are different. According to DFT calculations, the CN/NH vibrational cross angles of the dimer and trimer displayed in Figure 6B,F in water are bigger than 60° . If the angle changes to 0° , according to eq 2, the CN/NH energy transfer rate can be increased for more than 100%. This can be one very likely reason for the observed fast CN/NH energy transfer in the $1/5$ $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ solution.

In summary, both the CN/OH and CN/NH energy transfer measurements in the two relatively dilute NH_4SCN ($1/25$ and $1/10$) aqueous solutions give a $\text{NH}_4^+/\text{SCN}^-$ binding affinity $K = 18 \pm 4$, thus, supporting the assumption of one-to-one $\text{NH}_4^+/\text{H}_2\text{O}$ replacement. In the concentrated $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/5$ solution, both the CN/OH and the CN/NH energy transfer measurements show deviations (bigger $\text{NH}_4^+/\text{SCN}^-$ binding affinity values) compared to the results of the two dilute solutions. We attribute the deviations to the possible cation/anion complex structural changes because of ion clustering.

4. CONCLUDING REMARKS

The vibrational energy transfers among the cation (NH_4^+), the anion (SCN^-), and the water solvent molecule (H_2O) in three $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ ($= 1/25$, $1/10$, and $1/5$, molar ratio) solutions were simultaneously measured. It was found that in the solutions, NH_4^+ cations can directly bind to SCN^- anions. In the two relatively dilute ($1/10$ and $1/25$) solutions, the average $\text{NH}_4^+/\text{SCN}^-$ binding affinity (compared to that of $\text{H}_2\text{O}/$

SCN^-) is 18 ± 4 . The value indicates that $\sim 60\%$ of the cations directly bind to the anions in the $1/10$ $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ solution, and $\sim 43\%$ of the cations directly bind to the anions in the $1/25$ $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ solution. In the concentrated $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/5$ solution, the $\text{NH}_4^+/\text{SCN}^-$ binding affinity was determined to be larger than 18. The deviation in this concentrated solution was attributed to the probable structural changes in the solution because of significant ion clustering. We anticipate that the approach of simultaneously measuring energy transfers from one donor to competing acceptors as demonstrated in this work would be useful in other applications for determining short-range (<1 nm) and transient (<1 ns) intermolecular distances. We also urge precautions where many factors besides the donor/acceptor distance can also affect the vibrational energy transfer kinetics, e.g., energy mismatch, transition dipole moment, donor/acceptor relative orientation, local refractive indexes, and overlapping of combination band. Many control experiments must be conducted before quantitative results can be obtained.

■ ASSOCIATED CONTENT

Supporting Information

Figures and data about the vibrational lifetimes, the heat effects, pulse temporal shapes, the instrument response function, and energy transfer measurements on various samples are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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**Ion Association in Aqueous Solutions Probed through Vibrational Energy Transfers among
Cation, Anion and Water Molecules**

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Supporting materials

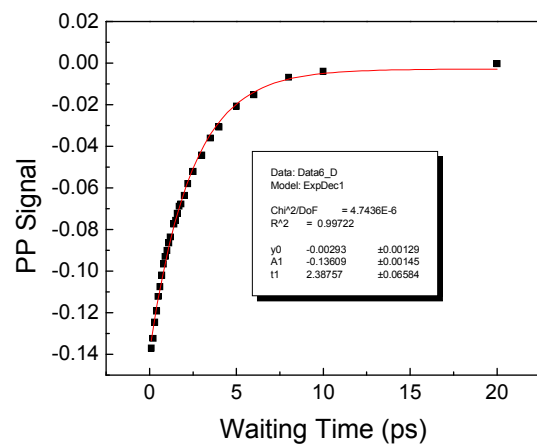


Figure S1. Experimental data (dots) and fitting (lines) for the SCN^- vibrational relaxation (1-2 transition) in the 0.05M KSCN H_2O solution. The SCN^- lifetime is determined to be $2.4 \pm 0.2 \text{ ps}$.

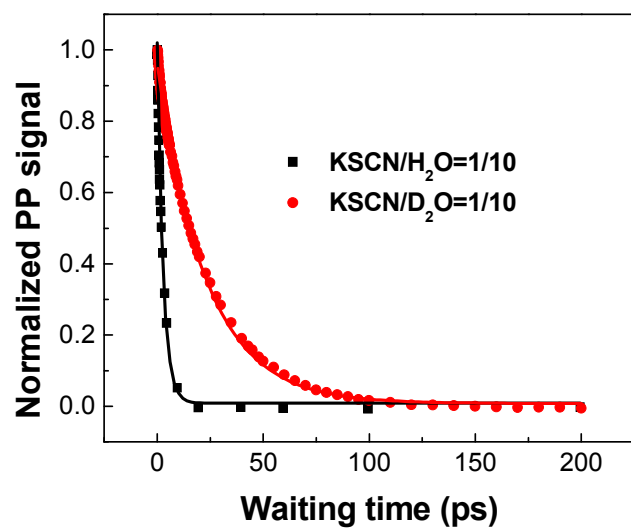


Figure S2. Vibrational decays of the CN stretch 1st excited state in the KSCN/H₂O (1/10) and KSCN/D₂O (1/10) solutions.

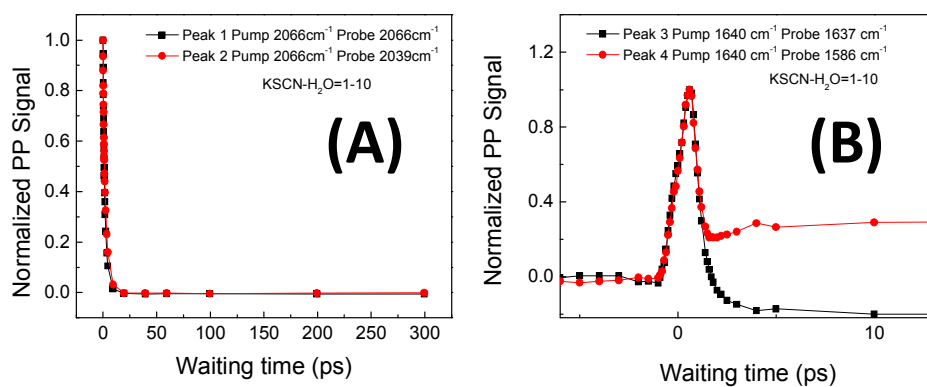


Figure S3. (A). The Normalized Pump Probe signal for Peak 1 and Peak 2. (B) The Normalized Pump Probe signal for peak 3 and 4. The maximum intensity was normalized to 1. The decays of peaks 1&2 are identical. The decays of peaks 3&4 are similar, but because of the heat effects, peak 3 shows absorption at long waiting times, and peak 4 shows bleaching at long waiting times.

Energy exchange between OH and NH bendings

The vibrational energy can also transfer from the OH bending to the NH bending in the NH_4SCN solution. Experimental results and calculations based on the energy exchange model

show that $\frac{1}{k_{\text{OH} \rightarrow \text{NH}}} = 4 \pm 0.8 \text{ ps}$, shown in fig.S4. Parameters are $\frac{1}{k_{\text{OH}}} = 1 \text{ ps}$, and

$$\frac{1}{k_{\text{NH}}} = 1.6 \text{ ps} \cdot \frac{k_{\text{NH} \rightarrow \text{OH}}}{k_{\text{OH} \rightarrow \text{NH}}} = 0.4 \text{ ps}$$

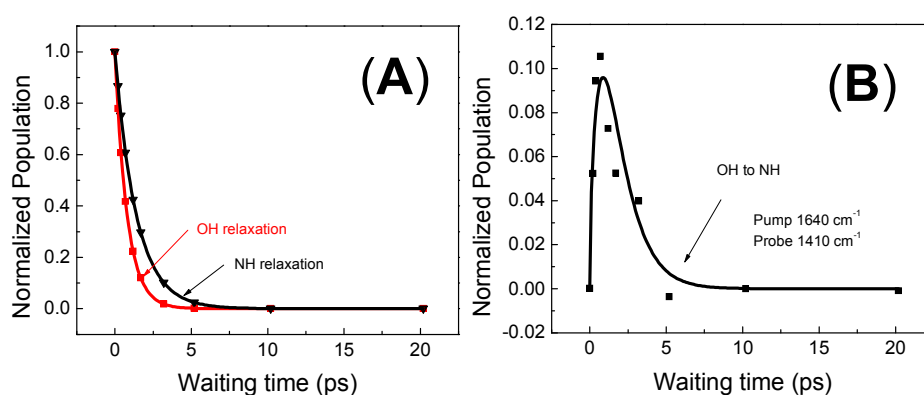


Figure S4. Experimental data (dots) and kinetic calculations (lines) for the OH bending relaxation, the NH bending relaxation, the OH to NH energy transfer in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O} = 1/10$ solution.

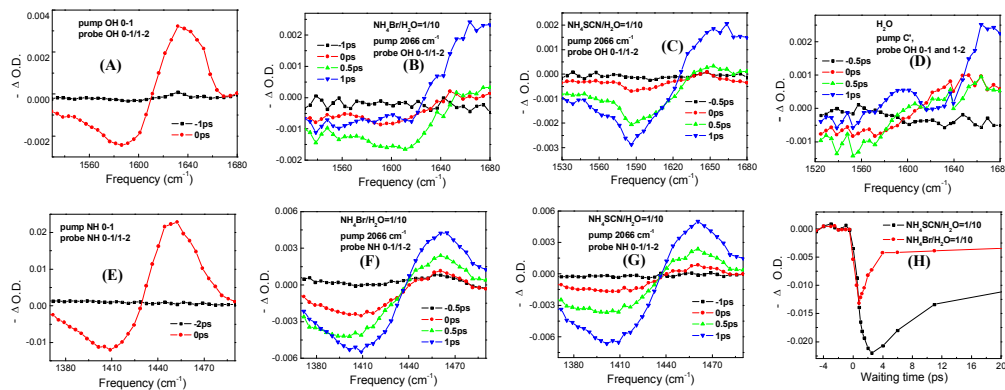


Figure S5. (A) Pump/probe spectra of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution by exciting the OH bending 0-1 transition at two delays. The absorption at $\sim 1580\text{ cm}^{-1}$ is the OH bending 1-2 transition. (B) Pump/probe spectra of the $\text{NH}_4\text{Br}/\text{H}_2\text{O}$ (1/10) solution by exciting C and C' at four delays. No absorption at $\sim 1580\text{ cm}^{-1}$ is observed. (C) Pump/probe spectra of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution by exciting the CN stretch, C and C' at four delays. The absorption at $\sim 1580\text{ cm}^{-1}$ is clearly observed. (D) Pump/probe spectra of pure H_2O by exciting C' at four delays. No apparent absorption at $\sim 1580\text{ cm}^{-1}$ is observed. (E) Pump/probe spectra of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution by exciting the NH bending 0-1 transition at two delays. The absorption at $\sim 1410\text{ cm}^{-1}$ is the NH bending 1-2 transition. (F) Pump/probe spectra of the $\text{NH}_4\text{Br}/\text{H}_2\text{O}$ (1/10) solution by exciting C and C' at 2066 cm^{-1} at four delays. The absorption at $\sim 1410\text{ cm}^{-1}$ is clearly observed. (G) Pump/probe spectra of the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ (1/10) solution by exciting the CN stretch, C and C' at 2066 cm^{-1} at four delays. The absorption at $\sim 1410\text{ cm}^{-1}$ is also clearly observed. (H) Time dependent rotational free pump/probe data of the $\text{NH}_4\text{Br}/\text{H}_2\text{O}$ (1/10) and $\text{NH}_4\text{Br}/\text{H}_2\text{O}$ (1/10) solutions by exciting the CN stretch, C and C' at 2066 cm^{-1} at four delays and detecting at 1410 cm^{-1} . The energy transfer is much more salient in the $\text{NH}_4\text{SCN}/\text{H}_2\text{O}$ solution.

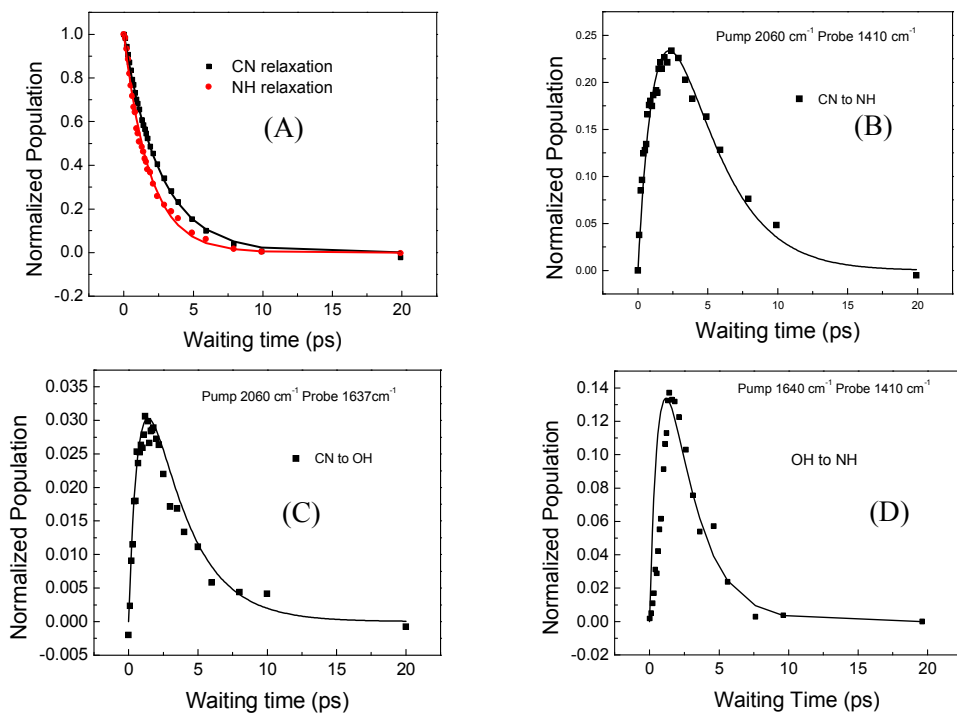


Figure S6. (A) The time dependent populations of the 1st excited states of CN stretch and OH bending, (B) the CN to NH energy transfer, (C) the CN to OH energy transfer, and (D) the OH to NH energy transfer in the NH₄SCN/H₂O (1/5) solution. Dots are data, and lines are calculations.

Calculation with parameters $\frac{1}{k''_{CN}} = 9.5 \text{ ps}$; $\frac{1}{k_{NH}} = 2.1 \text{ ps}$ for the CN/NH transfer yields

$\frac{1}{k_{CN \rightarrow NH}} = 3.7 \text{ ps}$. Calculation with parameters $\frac{1}{k'_{CN}} = 3.4 \text{ ps}$; $\frac{1}{k'_{OH}} = 0.7 \text{ ps}$ for the CN/OH

transfer yields $\frac{1}{k'_{CN \rightarrow OH}} = 16 \text{ ps}$. Calculation with parameters $\frac{1}{k_{OH}} = 1 \text{ ps}$; $\frac{1}{k_{NH}} = 2.5 \text{ ps}$ for

the OH/NH transfer yields $\frac{1}{k_{OH \rightarrow NH}} = 3.1 \text{ ps}$.

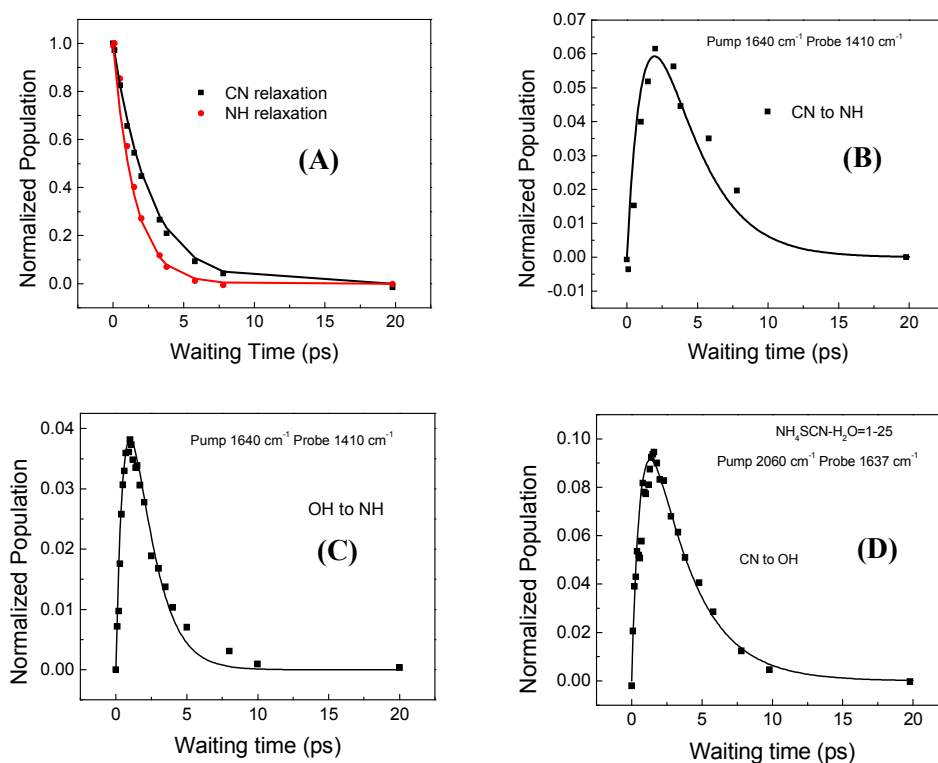


Figure S7. (A) The time dependent populations of the 1st excited states of CN stretch and OH bending, (B) the CN to NH energy transfer, (C) the OH to NH energy transfer, and (D) the CN to OH energy transfer in the NH₄SCN/H₂O (1/25) solution. Dots are data, and lines are calculations.

Calculation with parameters $\frac{1}{k''_{CN}} = 3.5 \text{ ps}$; $\frac{1}{k_{NH}} = 1.5 \text{ ps}$ for the CN/NH

transfer yields $\frac{1}{k_{CN \rightarrow NH}} = 12 \text{ ps}$. Calculation with parameters $\frac{1}{k'_{CN}} = 7.5 \text{ ps}$; $\frac{1}{k'_{OH}} = 0.7 \text{ ps}$

for the CN/OH transfer yields $\frac{1}{k'_{CN \rightarrow OH}} = 4.6 \text{ ps}$. Calculation with parameters

$\frac{1}{k_{OH}} = 0.8 \text{ ps}$; $\frac{1}{k_{NH}} = 1.5 \text{ ps}$ for the OH/NH transfer yields $\frac{1}{k_{OH \rightarrow NH}} = 9.5 \text{ ps}$.

Deconvolution with instrument response function

We introduced the instrument response function (IRF) as a Gaussian function

$$i(t) = \frac{1}{\tilde{\Delta}\sqrt{2\pi}} \exp(-\ln 2 \cdot (2(t-t_0)/\Delta)^2) \quad (S1)$$

where t_0 represents the zero point, Δ is full width at half maximum (FWHM) of the IRF, and

$\tilde{\Delta} = \Delta / (2\sqrt{2\ln 2})$. During the simulation, Δ was fixed as 0.7 ps which is estimated from the cross-correlation curve between the ps pump and fs probe pulses through sum frequency generation (SFG) method (see figure S8).

The convolution of an exponential function with this IRF results in an analytical expression¹:

$$\begin{aligned} c(t; k, t_0, \Delta) &= \exp(-kt) \oplus i(t) \\ &= \frac{1}{2} \exp(-kt) \exp(k(t_0 + \frac{k\tilde{\Delta}^2}{2})) \{1 + \operatorname{erf}(\frac{t - (t_0 + k\tilde{\Delta}^2)}{\sqrt{2}\tilde{\Delta}})\} \end{aligned} \quad (S2)$$

where k is the rate constant, $\oplus$ indicates convolution, and $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$ is the error function.

For any analytical equation that was used to calculate the vibrational lifetimes and energy transfer rates, we substituted $c(t; k, \mu, \Delta)$ for all the exponential functions of the equations to take into account the IRF.

The life time of the HOH bending mode was determined to be 0.8ps with the use of IRF. The result is slower than the reported value 170fs.²⁻³ Another group showed that the OH bending vibrational lifetime was 400fs.⁴ The different values from different groups are primarily caused by the way to treat the heat effect on the spectral observations. In this work, we assume that the heat effect appears (induced absorption at the 0-1 transition frequency) at very early time with a single exponential growth with a time constant of 0.8ps. After the removal of the heat effect, the OH bending relaxation time was determined to be 0.8 ± 0.2 ps. The result was shown in Figure S9A. Without removing the heat effect, the OH bending lifetime would be 200fs, similar to what was determined previously which seems not to consider the heat effect.²⁻³ The result was shown in Figure S9B.

The most severe effect of the long pump pulse on our experiments is the relatively big uncertainty of the experimentally determined transition dipole moment ratios among the CN stretch and the OH and NH bendings it causes. The lifetimes of the CN stretch is 2.8ps, that of OH bending is 0.8ps, and that of NH bending is 1.3 ps. The different lifetimes can cause the experimentally observed maximum 2D IR signals to be quite different from those 2D IR experimental responses if the pump pulse is extremely short. Simply using the maximum intensities from the diagonal peaks in 2D IR spectra to determine transition dipole moment ratios among the oscillators would cause a big uncertainty. To count for the effect of the relatively long pump pulse, we used eq.S2 to recover the maximum 2D IR responses for an assumed infinitely short pump pulse. The recovered values were then used in the calculations of the transition dipole moment ratios which were used in the normalization of the energy transfer populations. Different from that the maximum intensity of the diagonal peaks in 2D IR data is significantly affected by the pump pulse duration and the vibrational lifetime of the oscillator, those of the energy transfer cross peaks (CN/OH and CN/NH) are only very weakly affected because the relatively slow energy transfer rates. Considering these two factors, we found that the normalized CN/OH energy transfer population (the normalized intensity of the energy transfer cross peak) was over estimated by about 5% if IRF is not considered. That of the CN/NH transfer cross peak is essentially not affected. Figure S10-S13 show the calculation results for the cross peaks with and without IRF. Within experimental uncertainty, considering IRF doesn't affect the fitting results of the energy transfer rates. In analyzing the diagonal peaks' decays in the main text, we didn't include the very early rising signal because all the diagonal peaks can be described with a single exponential decay. Within experimental uncertainty, defining time 0 at the time when experimentally observed

maximum signal appears in the kinetic analysis does not cause any noticeable difference in the final determined energy transfer rates.

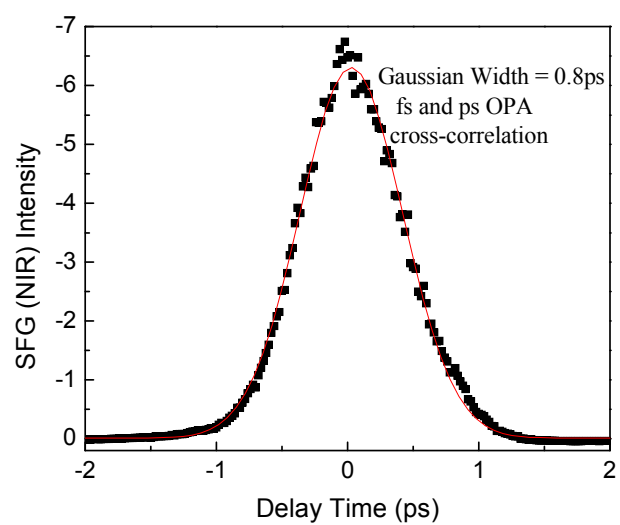


Figure S8. The cross-correlation curve between the ps pump and fs probe pulses obtained by measuring the SFG signal of the two pulses in AgGaS₂ crystal.

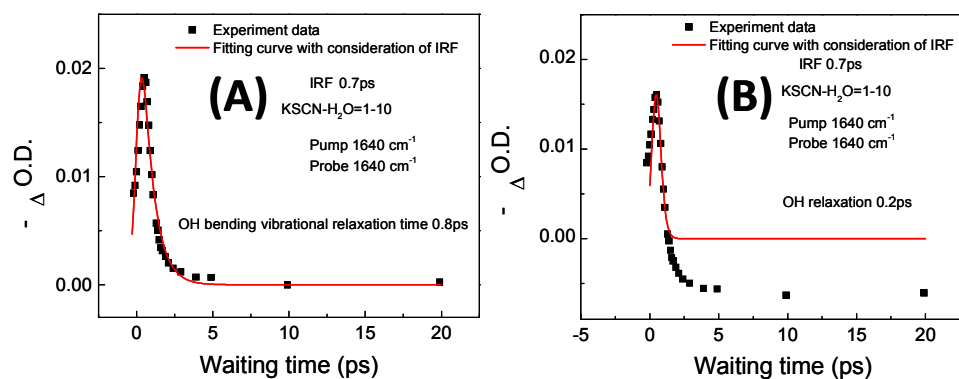


Figure S9. The OH bending vibrational relaxation dynamics (A) Experiment data with subtraction of heat (dots). The heat effect is assumed to be a single exponential growth with a time constant 800fs. The line is calculation with IRF with a pulse width of 0.7ps. The OH bending relaxation time is determined to be 0.8ps. (B) Experiment data without subtraction of heat (dots). The line is calculation with IRF with a pulse width of 0.7ps. The OH bending relaxation time is determined to be 0.2ps.

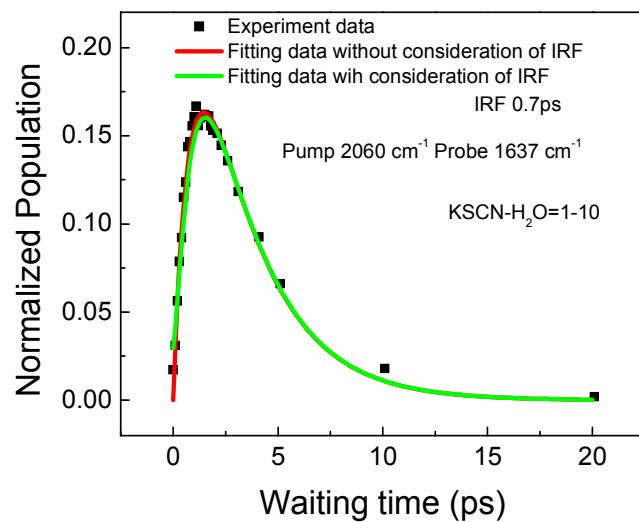


Figure S10. The fitting curves for energy transfer peak for solution (KSCN-H₂O=1-10).

Dots are the experiment data, and lines are the fitting results. Calculation with parameters

$$\frac{1}{k_{CN}} = 30 \text{ ps}; \frac{1}{k_{OH}} = 0.85 \text{ ps} \text{ for the CN/OH transfer yields } \frac{1}{k_{CN \rightarrow OH}} = 3.1 \text{ ps}, \text{ without IRF;}$$

$$\text{Calculation with parameters } \frac{1}{k_{CN}} = 30 \text{ ps}; \frac{1}{k_{OH}} = 0.85 \text{ ps} \text{ for the CN/OH transfer yields}$$

$$\frac{1}{k_{CN \rightarrow OH}} = 3.1 \text{ ps} \text{ with IRF with a } \Delta \text{ of } 0.7 \text{ ps.}$$

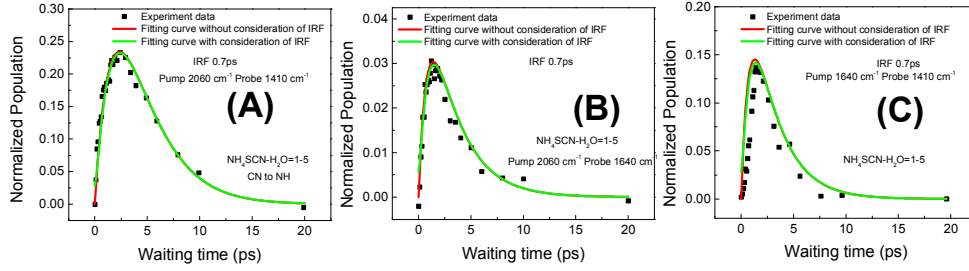


Figure S11. The fitting curves for energy transfer peaks for solution ($\text{NH}_4\text{SCN-H}_2\text{O}=1-5$). (A)

the CN to NH energy transfer; (B) the CN to OH energy transfer; and (C) the OH to NH energy

transfer. Dots are the experiment data, and lines are the fitting results. Calculation with

parameters $\frac{1}{k''_{\text{CN}}} = 9.5 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 2.1 \text{ ps}$ for the CN/NH transfer yields $\frac{1}{k_{\text{CN} \rightarrow \text{NH}}} = 3.7 \text{ ps}$,

without IRF; Calculation with parameters $\frac{1}{k''_{\text{CN}}} = 9.5 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 2.1 \text{ ps}$ for the CN/NH

transfer yields $\frac{1}{k_{\text{CN} \rightarrow \text{NH}}} = 3.7 \text{ ps}$ with IRF with a Δ of 0.7 ps. Calculation with parameters

$\frac{1}{k'_{\text{CN}}} = 3.4 \text{ ps}$; $\frac{1}{k'_{\text{OH}}} = 0.8 \text{ ps}$ for the CN/OH transfer yields $\frac{1}{k'_{\text{CN} \rightarrow \text{OH}}} = 16 \text{ ps}$, without IRF;

Calculation with parameters $\frac{1}{k'_{\text{CN}}} = 3.4 \text{ ps}$; $\frac{1}{k'_{\text{OH}}} = 0.8 \text{ ps}$ for the CN/OH transfer yields

$\frac{1}{k'_{\text{CN} \rightarrow \text{OH}}} = 16 \text{ ps}$ with IRF with a Δ of 0.7 ps. Calculation with parameters

$\frac{1}{k_{\text{OH}}} = 1 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 2.5 \text{ ps}$ for the CN/NH transfer yields $\frac{1}{k_{\text{OH} \rightarrow \text{NH}}} = 3.1 \text{ ps}$, without IRF;

Calculation with parameters $\frac{1}{k_{\text{OH}}} = 1 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 2.5 \text{ ps}$ for the OH/NH transfer yields

$\frac{1}{k_{\text{OH} \rightarrow \text{NH}}} = 3.1 \text{ ps}$ with IRF with a Δ of 0.7 ps.

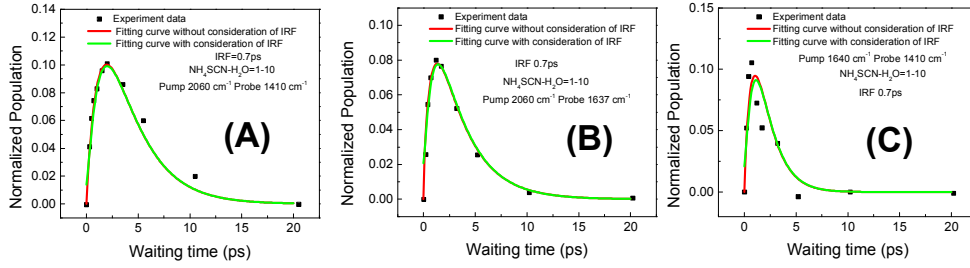


Figure S12. The fitting curves for energy transfer peaks for solution ($\text{NH}_4\text{SCN-H}_2\text{O}=1-10$). (A)

the CN to NH energy transfer, (B) the CN to OH energy transfer, and (C) the OH to NH energy

transfer. Dots are the experiment data, and lines are the fitting results. Calculation with

parameters $\frac{1}{k''_{\text{CN}}} = 5.2 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.35 \text{ ps}$ for the CN/NH transfer yields $\frac{1}{k_{\text{CN} \rightarrow \text{NH}}} = 7.0 \text{ ps}$,

without IRF; Calculation with parameters $\frac{1}{k''_{\text{CN}}} = 5.2 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.35 \text{ ps}$ for the CN/NH

transfer yields $\frac{1}{k_{\text{CN} \rightarrow \text{NH}}} = 7.0 \text{ ps}$ with IRF with a Δ of 0.7 ps. Calculation with parameters

$\frac{1}{k'_{\text{CN}}} = 5.5 \text{ ps}$; $\frac{1}{k'_{\text{OH}}} = 0.8 \text{ ps}$ for the CN/OH transfer yields $\frac{1}{k'_{\text{CN} \rightarrow \text{OH}}} = 6.3 \text{ ps}$, without IRF;

Calculation with parameters $\frac{1}{k'_{\text{CN}}} = 5.5 \text{ ps}$; $\frac{1}{k'_{\text{OH}}} = 0.8 \text{ ps}$ for the CN/OH transfer yields

$\frac{1}{k'_{\text{CN} \rightarrow \text{OH}}} = 6.2 \text{ ps}$ with IRF with a Δ of 0.7 ps. Calculation with parameters

$\frac{1}{k_{\text{OH}}} = 1 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.6 \text{ ps}$ for the OH/NH transfer yields $\frac{1}{k_{\text{OH} \rightarrow \text{NH}}} = 4.0 \text{ ps}$, without IRF;

Calculation with parameters $\frac{1}{k_{\text{OH}}} = 1 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.6 \text{ ps}$ for the OH/NH transfer yields

$\frac{1}{k_{\text{OH} \rightarrow \text{NH}}} = 4.0 \text{ ps}$ with IRF with a Δ of 0.7 ps.

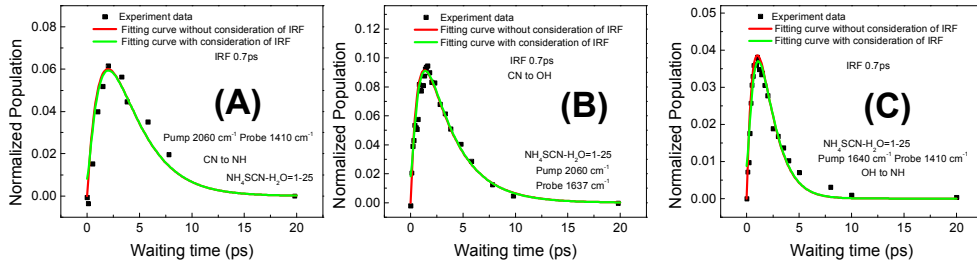


Figure S13. The fitting curves for energy transfer peaks for solution ($\text{NH}_4\text{SCN-H}_2\text{O}=1-25$). (A)

the CN to NH energy transfer; (B) the CN to OH energy transfer; and (C) the OH to NH energy

transfer. Dots are the experiment data, and lines are the fitting results. Calculation with

parameters $\frac{1}{k''_{\text{CN}}} = 3.5 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.5 \text{ ps}$ for the CN/NH transfer yields $\frac{1}{k_{\text{CN} \rightarrow \text{NH}}} = 12.0 \text{ ps}$,

without IRF; Calculation with parameters $\frac{1}{k''_{\text{CN}}} = 3.5 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.5 \text{ ps}$ for the CN/NH

transfer yields $\frac{1}{k_{\text{CN} \rightarrow \text{NH}}} = 12.0 \text{ ps}$ with IRF with a Δ of 0.7 ps. Calculation with parameters

$\frac{1}{k'_{\text{CN}}} = 7.5 \text{ ps}$; $\frac{1}{k'_{\text{OH}}} = 0.7 \text{ ps}$ for the CN/OH transfer yields $\frac{1}{k'_{\text{CN} \rightarrow \text{OH}}} = 4.6 \text{ ps}$, without IRF;

Calculation with parameters $\frac{1}{k'_{\text{CN}}} = 7.5 \text{ ps}$; $\frac{1}{k'_{\text{OH}}} = 0.7 \text{ ps}$ for the CN/OH transfer yields

$\frac{1}{k'_{\text{CN} \rightarrow \text{OH}}} = 4.6 \text{ ps}$ with IRF with a Δ of 0.7 ps. Calculation with parameters

$\frac{1}{k_{\text{OH}}} = 0.8 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.5 \text{ ps}$ for the OH/NH transfer yields $\frac{1}{k_{\text{OH} \rightarrow \text{NH}}} = 9.5 \text{ ps}$, without IRF;

Calculation with parameters $\frac{1}{k_{\text{OH}}} = 0.8 \text{ ps}$; $\frac{1}{k_{\text{NH}}} = 1.5 \text{ ps}$ for the OH/NH transfer yields

$\frac{1}{k_{\text{OH} \rightarrow \text{NH}}} = 9.5 \text{ ps}$ with IRF with a Δ of 0.7 ps.

Reference:

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