# Nonresonant Energy Transfers Independent on the Phonon Densities in Polyatomic Liquids

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#### **Supporting Information**



**ABSTRACT:** Energy-gap-dependent vibrational-energy transfers among the nitrile stretches of KSCN/KS<sup>13</sup>CN/KS<sup>13</sup>C<sup>15</sup>N in  $D_2O$ , DMF, and formamide liquid solutions at room temperature were measured by the vibrational-energy-exchange method. The energy transfers are slower with a larger energy donor/acceptor gap, independent of the calculated instantaneous normal mode ("phonons" in liquids) densities or the terahertz absorption spectra. The energy-gap dependences of the nonresonant energy transfers cannot be described by phonon compensation mechanisms with the assumption that phonons are the instantaneous normal modes of the liquids. Instead, the experimental energy-gap dependences can be quantitatively reproduced by the dephasing mechanism. A simple theoretical derivation shows that the fast molecular motions in liquids randomize the modulations on the energy donor and acceptor by phonons and diminish the phonon compensation efficiency on energy transfer. Estimations based on the theoretical derivations suggest that, for most nonresonant intermolecular vibrational-energy transfers in liquids with energy gaps smaller than the thermal energy, the dephasing mechanism dominates the energy-transfer process.

#### 1. INTRODUCTION

In nature, energy transfer from one level of one molecule to another level of another molecule is ubiquitous. This process is typically called nonresonant energy transfer. In the condensed phase, the energy values of the donor and acceptor have certain distributions because of molecular motions and interactions. Therefore, being "nonresonant" refers to the fact that the central value of the donor energy distribution is different from that of the acceptor. For the transfer process to occur, the total energy needs to be conserved. It is traditionally believed that the gap between the central energy values of the donor and acceptor is compensated by phonons available in the bath.<sup>1,2</sup> If the energy gap is close to that of the most abundant phonons in the bath, the energy-transfer system needs to pick up one phonon from the bath with energy matching the gap if the energy of the donor is smaller than that of the acceptor or emit one phonon into the bath if the donor has a higher energy than the acceptor. If the energy gap is much larger than the energies of the most abundant phonons, two or more phonons can be involved in the energy-transfer process. This idea was applied to explain electronic energy transfers in crystalline solids.<sup>1-3</sup> Later on, it was extended to explain vibrational-energy relaxations and transfers in liquids.<sup>4-6</sup> Close examination of the literature identifies discrepancies. For the one-phonon process, the majority of theoretical approaches use the first-order coupling matrix<sup>1</sup>

$$k_{\rm DA} = V_{\rm DA}^{2} V_{\rm s-b}^{\prime} \rho_{\Delta E_{\rm DA}}^{2} N \tag{1}$$

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where  $k_{\rm DA}$  is the energy-transfer rate constant from the donor (D) to the acceptor (A).  $\Delta E_{\rm DA}$  is the donor/acceptor energy gap.  $V_{\rm DA}$  is the coupling between D and A.  $V'_{\rm s-b}$  is the systembath coupling.  $\rho_{\Delta E_{\rm DA}}$  is the phonon density of the bath at the energy gap  $\Delta E_{\rm DA}$ .  $N = [\exp(|\Delta E_{\rm DA}|/RT) - 1]^{-1} + 1$  for the emission process, and  $N = [\exp(|\Delta E_{\rm DA}|/RT) - 1]^{-1}$  for the absorption process. However, another theoretical approach<sup>2</sup> states that the first-order coupling matrix is very close to zero. Therefore, the second-order coupling matrix rather than the first-order coupling matrix is needed to describe the onephonon process<sup>7</sup>

$$k_{\rm DA} = V_{\rm DA}^{2} V_{\rm s-b}^{2} \frac{\rho_{\Delta E_{\rm DA}}}{\Delta E_{\rm DA}^{2}} N$$
<sup>(2)</sup>

The two energy-transfer equations (eqs 1 and 2) to describe the same process are similar except that the term  $\Delta E_{DA}^2$ appears in the denominator of eq 2, making the prediction of the gap dependence of the energy-transfer rate different from that using eq 1.

In addition to the phonon compensation mechanisms, another mechanism can govern the nonresonant energy transfers in condensed phases. In a condensed phase, the energy of a molecule is a distribution rather than a single value. Consequently, for an energy-transfer system with different donor/acceptor central energy values, there is always some chance that the energy distributions of the donor and acceptor can overlap. Energy can thus transfer between the donor and acceptor resonantly through the overlapping portion in a manner similar to Förster energy transfer. We call this "the dephasing mechanism".<sup>7</sup> According to our previous studies,<sup>7,8</sup> the energy-transfer rate constant of the dephasing mechanism can be expressed as

$$k_{\rm DA} = \frac{2}{1 + e^{\Delta \omega/RT}} V^2 \frac{\frac{1}{\tau}}{(\Delta \omega)^2 + 4V^2 + \tau^{-2}}$$
(3)

where  $\Delta \omega$  ( $\Delta \omega = \omega_{\rm A} - \omega_{\rm D}$ ) is the donor/acceptor (D/A) energy gap, V is the D/A coupling strength, and  $\tau$  is the dephasing time of D/A coherence. If the energy transfer is through the dephasing mechanism, the rate is lower with a larger gap because the resonant overlap is smaller, independent of the phonon density. For any nonresonant energy transfer in a condensed phase, both dephasing and phonon compensation mechanisms play roles simultaneously, as a donor molecule and an acceptor molecule that have different frequencies can fluctuate to have the same energy by dephasing and resonantly transfer energy through the dephasing mechanism or directly nonresonantly transfer energy through phonon compensation before they fluctuate to have the same energy.

For electronic energy transfers in liquids, the line width of either donor or acceptor is typically broader than 6 nm (>100 cm<sup>-1</sup>, close to the thermal energy of 200 cm<sup>-1</sup> at room temperature). The spectra of donor and acceptor overlap significantly for relatively small central frequency differences (<200 cm<sup>-1</sup>). It is therefore the dephasing mechanism that works well, and the Förster approach,<sup>9–11</sup> in which the dephasings of the donor and acceptor are uncorrelated so that the spectral overlap can be used to estimate the energy-transfer rate,<sup>7</sup> is typically used. If the gap is large, the spectral overlap is small, and the energy transfer through the dephasing mechanism is slow, phonon compensation can still play a very minor role because now it can require multiple phonons to

compensate the gap, which can be very slow. For electronic energy transfers in solids, the line widths can be very narrow, and the phonon compensation mechanism can be dominant.<sup>2</sup>

Energy transfers in the molecular vibrational regime are different from those in the electronic regime. The line width is much narrower. A typical vibrational mode (except those strongly H-bonded species, e.g., OH stretch) in a liquid has a line width of  $\sim 20$  cm<sup>-1</sup> or smaller. If the gap between the central energy values of the donor and acceptor is close to the thermal energy at room temperature, 200  $\text{cm}^{-1}$ , on one hand, the spectral overlap is very small and therefore the energy transfer through the dephasing mechanism must be very slow. On the other hand, the bath can provide a sufficiently large number of phonons at the energy of the gap so that onephonon compensated energy transfer can occur in such a system. Therefore, nonresonant vibrational-energy transfers were typically considered as occurring through the phonon compensation mechanism even in liquids where "phonons" are those instantaneous normal modes,<sup>4,12</sup> and the dephasing mechanism was not considered.

The general ideas about energy transfers under various conditions as described above have been used to explain experimental observations for decades.<sup>4,5</sup> However, very few experiments have been able to unambiguously test these ideas. One main obstacle is that the key experiments for testing different energy-transfer mechanisms, namely, energy-gapdependent energy-transfer experiments, are practically difficult to perform because "experimentally it is difficult to somehow change the frequency of the energy gap but keep all other features of the system the same."<sup>1</sup> Because of the experimental difficulties, many critical problems about nonresonant molecular energy transfer in condensed phases remain open, such as how to predict the relative importance of the two energytransfer mechanisms. Our previous experiments showed that the phonon compensation mechanism plays an important role in nonresonant energy transfers between the nitrile stretches of KSCN and  $K^{13}C^{15}N'$  (with a gap of 75 cm<sup>-1</sup>) and those of KSCN and  $K^{13}CN$  (with a gap of 48 cm<sup>-1</sup>) in potassium thiocyanate crystals. However, in liquids, for the same energytransfer processes, the dephasing mechanism, instead of the phonon compensation mechanism, is important.<sup>7</sup> In this work, by combining energy-gap-dependent energy-transfer measurements, calculations of instantaneous normal modes, and theoretical derivations, we take one step further to investigate the relative importance of the dephasing mechanism and the phonon (instantaneous normal mode) compensation mechanisms in nonresonant vibrational-energy transfers in liquids and possible reasons that lead to this relative importance.

#### 2. MATERIALS AND METHODS

**2.1. Materials.** Unless otherwise specified, chemicals were purchased from Sigma-Aldrich and used without further purification.  $KS^{13}C^{15}N$  and  $KS^{13}CN$  were purchased from Cambridge Isotope Laboratory. D<sub>2</sub>O was obtained from C/D/ N Isotopes Inc. Formamide was obtained from EMD Millipore.

**2.2. Methods.** A picosecond amplifier (~1 ps) and a femtosecond amplifier (38 fs) were synchronized with the same seed pulse. The picosecond amplifier pumped an optical parametric amplifier to produce ~0.8 ps IR pulses (varying from 0.7 to 0.9 ps at different frequencies) with a bandwidth of 10-35 cm<sup>-1</sup> in the tunable frequency range from 400 to 4000 cm<sup>-1</sup> with an energy of  $1-40 \mu J/pulse$  at 1 kHz. Light from the femtosecond amplifier was used to generate a high-intensity

mid-IR and terahertz supercontinuum pulse with a duration of <100 fs in the frequency range from <10 cm<sup>-1</sup> to >3500 cm<sup>-1</sup> at 1 kHz.13 In experiments, the picosecond IR pulse was the excitation beam (the excitation power was adjusted based on need, and the focus spot varied from 100 to 500  $\mu$ m). The supercontinuum pulse was the detection beam, which was frequency-resolved by a spectrograph (resolution of  $1-3 \text{ cm}^{-1}$ depending on frequency), yielding the detection axis of a 2D IR spectrum. Two polarizers were added into the path of the detection beam to selectively measure the parallel- or perpendicular-polarized signal relative to the excitation beam. Vibrational lifetimes were obtained from the transition signal of rotation-free CN stretch 0-1 (from the CN-stretch ground state to its first excited state) or 1-2 (from the CN stretch first excited state to its second excited state)  $P_{\text{life}} = P_{\parallel} + 2 \times P_{\perp}$ , where  $P_{\parallel}$  and  $P_{\perp}$  are the parallel and perpendicular data, respectively, obtained from experiments in which the polarization of the excitation beam was parallel  $(P_{\parallel})$  and perpendicular  $(P_{\perp})$  to that of the detection beam. Vibrational-energy-transfer rate constants were obtained from the vibrational-energy-exchange method and the resonant energy-transfer-induced anisotropy decay method.<sup>14–17</sup>

Terahertz absorption spectra were obtained on a home-built ultrafast broadband terahertz spectrometer.<sup>13,18</sup>

**2.3.** MD Simulations and Instantaneous Normal Mode (INM). In the MD simulations, the initial spatial distributions of the molecules and ions were set up to be random. The SPC/E model<sup>19</sup> was used for  $D_2O$  water. The OPLS force fields from the GROMACS package<sup>20</sup> were used for the formamide and dimethylformamide (DMF) solvents. Cubic periodic boundary boxes were used in the simulations. The SCN<sup>-</sup> model was taken from a previous work.<sup>21</sup>

For each sample, a 2-ns NPT ensemble equilibration was carried out to generate the proper size of the simulation box, and then enough samples were collected for INM analysis. The sample sizes and compositions are listed in Table 1. The

| Table | 1. Details | of the | Simu | lation | Boxes |
|-------|------------|--------|------|--------|-------|
|       |            |        |      |        |       |

| composition                                                  | number of solvent<br>molecules | box size<br>(Å) |
|--------------------------------------------------------------|--------------------------------|-----------------|
| KSCN/KS <sup>13</sup> C <sup>15</sup> N/formamide<br>(1:1:8) | 500                            | 33.23           |
| KSCN/KS <sup>13</sup> CN/formamide<br>(1:1:8)                | 500                            | 33.23           |
| KSCN/KS <sup>13</sup> CN/D <sub>2</sub> O (1:1:4.8)          | 500                            | 31.95           |
| $KSCN/KS^{13}C^{15}N/D_2O$ (1:1:4.8)                         | 500                            | 31.95           |
| KSCN/KS <sup>13</sup> CN/DMF (1:1:16)                        | 500                            | 42.13           |
| KSCN/KS <sup>13</sup> C <sup>15</sup> N/DMF (1:1:16)         | 500                            | 42.13           |

equations of motion were integrated using the velocity Verlet integration scheme<sup>22</sup> with a time step of 2 fs. For each *NPT* simulation, the temperature was weakly coupled to a bath with Nosé–Hoover thermostats<sup>23,24</sup> at 298 K with a relaxation time of 0.1 ps. The weak coupling Berendsen scheme was used to control the system pressure at 1 atm with a coupling time constant of 1 ps.<sup>25</sup> Long-range Coulombic forces were calculated using the particle-mesh Ewald method.<sup>26</sup> The Lorentz–Berthelot rules<sup>22</sup> were used as the combination rule for the Lennard-Jones potential parameters. The nonbonded van der Waals interactions were truncated at 12 Å using switching functions. Minimum image conditions<sup>22</sup> were used. All simulations were performed using the GROMACS 4.3 simulation package.<sup>20</sup> The instantaneous normal mode (INM) analysis<sup>12,27</sup> was derived from the Hessian matrices. The second derivatives of the potential energy  $[E(\mathbf{R})]$  for the 50 configurations from molecular dynamics simulations were calculated with respect to the mass-weighted atomic coordinates. The configurations were collected every 10-ps frequency. The INM frequencies  $\omega_i(\mathbf{R})$  (i = 1, ..., 3N) of samples with N atoms were obtained by diagonalizing the  $3N \times 3N$  Hessian matrix. The density of states (DOS) of INMs is written as the ensemble average,  $D(\omega) = \langle \sum_{i=1}^{3N} \delta[\omega - \omega_i(\mathbf{R})]/3N \rangle$ .

#### 3. RESULTS AND DISCUSSION

3.1. FTIR, Terahertz, Neutron Scattering, and Instantaneous Normal Mode Spectra. The nonresonant energytransfer systems studied were composed of 1:1 KSCN/KS<sup>13</sup>CN and 1:1 KSCN/KS13C15N in formamide, DMF, and D2O solutions, as well as 1:1 KS<sup>13</sup>CN/KS<sup>13</sup>C<sup>15</sup>N in DMF solutions. In the vibrational-energy-transfer experiments, the energy donors and acceptors were the nitrile stretches CN, <sup>13</sup>CN, and <sup>13</sup>C<sup>15</sup>N of the anions. Isotope labeling shifts the vibrational frequency of the nitrile stretch but not other molecular properties (transition dipole moment, phonon density, and molecular interaction strength) that might affect the energytransfer rate. As displayed in Figure 1, the vibrational frequency of the nitrile stretch 0-1 transition of SCN<sup>-</sup> is 2061 cm<sup>-1</sup> in formamide solution, 2057 cm<sup>-1</sup> in DMF solution, and 2066  $cm^{-1}$  in D<sub>2</sub>O solution. Those of S<sup>13</sup>CN<sup>-</sup> and S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> are red shifted by 48 and 75 cm<sup>-1</sup>, respectively, in each solvent because of their heavier masses. In each solvent, the widths of the nitrile stretch peaks with different isotopes are identical, indicating that the possible disruption of solute/solvent interactions caused by isotope labeling is negligible. Normalized with respect to the molar ratio, the heights of the nitrile peaks in each solvent are also the same, indicating that the possible change in the nitrile stretch 0-1 transition dipole moment caused by isotope labeling is also negligible. In addition, isotope labeling is not expected to change the internal vibrational modes of SCN<sup>-</sup> at frequencies below 100 cm<sup>-1</sup>, where the energy gaps among the nitrile stretches are, because no internal vibrational modes of the SCN<sup>-</sup> reside at such low frequencies. According to our DFT calculations, the lowest vibrational frequency of a SCN<sup>-</sup> ion is about 440 cm<sup>-1</sup>. Raman and neuron scattering spectra in Figure 1H,I show that even the frequencies of lattice motions (phonons) of potassium thiocyanate crystals are hardly affected by isotope labeling.

The three solvents have very different molecular structures, different terahertz absorption spectra (Figure 2) at frequencies below 100 cm<sup>-1</sup>, and different instantaneous normal mode distributions (Figure 3). In the three solvents, the widths of the nitrile stretch peaks are also different. The full width at half-maximum (fwhm) is ~28 cm<sup>-1</sup> in formamide, ~15 cm<sup>-1</sup> in DMF, and ~29 cm<sup>-1</sup> in D<sub>2</sub>O. The different line widths reflect the different solute/solvent interactions in the solutions.

**3.2. Energy-Gap-Dependent Vibrational-Energy Transfers.** As discussed above, in each solvent, the only difference among the vibrational-energy transfers between any two nitrile stretches of KSCN/KS<sup>13</sup>CN/KS<sup>13</sup>C<sup>15</sup>N is the energy gap. Other parameters that can affect the energy-transfer kinetics remain essentially constant in solutions with potassium thiocyanate labeled with different isotopes. Therefore, measuring the vibrational-energy-transfer rates between two nitrile stretches of anions labeled with different isotopes allows the energy-gap dependence of the energy transfers to be tested

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**Figure 1.** (A) FTIR spectrum of the CN and <sup>13</sup>CN stretches of SCN<sup>-</sup> and S<sup>13</sup>CN<sup>-</sup> in a 1:1 KSCN/KS<sup>13</sup>CN formamide solution with a 1:4 salt molar ratio at room temperature. The energy donor/acceptor gap is 48 cm<sup>-1</sup>. Top: Illustration of energy transfer from SCN<sup>-</sup> to S<sup>13</sup>CN<sup>-</sup> anion. (B) FTIR spectrum of the CN and <sup>13</sup>C<sup>15</sup>N stretches of SCN<sup>-</sup> and S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> in a KSCN/KS<sup>13</sup>C<sup>15</sup>N = 1/1.05 formamide solution with a 1:4 salt molar ratio at room temperature. The energy donor/acceptor gap is 75 cm<sup>-1</sup>. Top: Illustration of energy transfer from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> anion. Yellow balls represent S, gray balls represent C, and blue balls represent N. (C–E) FTIR spectra of (C) KS<sup>13</sup>CN/KS<sup>13</sup>C<sup>15</sup>N = 1.06/1, (D) KSCN/KS<sup>13</sup>CN = 1.04/1, and (E) KSCN/KS<sup>13</sup>C<sup>15</sup>N = 1/1.02 showing the nitrile stretch 0–1 transition peaks in DMF solution with 1:8 salt molar ratio at room temperature. (F,G) FTIR spectra of (F) KSCN/KS<sup>13</sup>CN = 1.05/1 and (G) KSCN/KS<sup>13</sup>C<sup>15</sup>N = 1.06/1 showing the nitrile stretch 0–1 transition peaks in D<sub>2</sub>O solution with 1:2.4 salt molar ratio at room temperature. (I) Neutron scattering spectra of KSCN and KS<sup>13</sup>C<sup>15</sup>N crystals at 5 K.

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directly. Because solutions with different solvents have different instantaneous normal mode distributions, comparisons among the energy-gap dependences in different solutions can also provide information about whether the nonresonant vibrational-energy transfers between two nitrile stretches depend on the instantaneous normal modes. <sup>0.8</sup> (A)

0.6

0.4

0.2

0.0 ∟ 20

OD (A. U.)

Formamide

60

Frequency (cm<sup>-1</sup>)

80



100

0.2

0.0 ∟ 20

60

Frequency (cm<sup>-1</sup>)



100

0.:

0.0 ∟ 20



60

Frequency (cm<sup>-1</sup>)

80

**Figure 3.** (A–C) Calculated phonon density of states of INM of 1:1 KSCN/KS<sup>13</sup>CN (black lines) and 1:1 KSCN/KS<sup>13</sup>C<sup>15</sup>N (red lines) (A) in a DMF solution with a 1:8 salt molar ratio, (B) in a D<sub>2</sub>O solution with a 1:2.4 salt molar ratio, and (C) in a formamide solution with a 1:4 salt molar ratio at room temperature. Isotope substitutions of <sup>12</sup>C and <sup>14</sup>N by <sup>13</sup>C and <sup>15</sup>N do not change the density of states of INM. (D) Calculated phonon density of states of the instantaneous normal mode of 1:1 KSCN/KS<sup>13</sup>CN in a DMF solution with a 1:8 salt molar ratio, in a D<sub>2</sub>O solution with a 1:2.4 salt molar ratio at room temperature.

To measure the energy transfers among the nitrile stretches, we used the vibrational-energy-exchange 2D IR method<sup>14,16,17</sup> with which the energy-transfer rate constants  $k_{CN \rightarrow {}^{13}C^{15}N}$  from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> with an energy gap of 75 cm<sup>-1</sup> and  $k_{CN} \rightarrow {}^{13}CN$  from SCN<sup>-</sup> to S<sup>13</sup>CN<sup>-</sup> with an energy gap of 48 cm<sup>-1</sup> in different solutions can be determined directly. Figure 4A displays three waiting-time-dependent 2D IR spectra of the 1:1 KSCN/KS13C15N formamide solution with a 1:4 salt/solvent molar ratio. At 0 ps, there are only two peak pairs on the diagonal. Red peaks 1 and 3 are the 0-1 (from the ground state to the first excited state) transition (both bleaching and stimulated emission) signals of the CN and <sup>13</sup>C<sup>15</sup>N stretches, respectively, two blue peaks 2 and 4 are their corresponding 1-2 (from the first to the second excited state) absorption signals, which shift to lower frequencies along the  $\omega_3$  axis because of vibrational anharmonicities. With an increase in waiting time, vibrational energy begins to be exchanged between SCN<sup>-</sup> and S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> anions. As a result of energy exchange, two crosspeak pairs (peaks 5-8) grow in the 2D IR spectra (50 and 100 ps). Peaks 5 and 6 arise from the energy transfer from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup>, and peaks 7 and 8 are generated by the reverse energy-transfer process from S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> to SCN<sup>-</sup>. Peaks 5 and 6 are larger than peaks 7 and 8 because of the detailed balance principle.7,28 Simultaneous analyses of the time-dependent intensities of peaks 2, 4, 6, and 8 based on the vibrationalenergy-exchange kinetic model<sup>14,16,17</sup> show that the energytransfer time  $(1/k_{CN\rightarrow 13}C^{15}N)$  from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> is 290 ± 30 ps. A description of the kinetic model is provided in the Supporting Information. Data and calculations are displayed in Figure 4C,D.

The energy transfer from SCN<sup>-</sup> to  $S^{13}$ CN<sup>-</sup> in the 1:1 KSCN/KS<sup>13</sup>CN formamide solution was also measured. At 50 and 100 ps, cross-peaks 6 and 7 in the 2D IR spectra of Figure 4B have larger intensities than those in Figure 4A at the same waiting times (the relatively smaller cross-peaks 5 and 8 in Figure 4B are because of cancellation by peaks 2 and 3,

respectively, of opposite signs). This observation indicates that the vibrational-energy transfer between the nitrile stretches is faster with a smaller energy donor/acceptor gap, because the growth of the cross-peaks indicates how fast the energy transfer occurs. Kinetic analyses (Figure 4E,F) show that the energy transfer time  $(1/k_{\rm CN}\rightarrow^{13}{\rm CN})$  from SCN<sup>-</sup> to S<sup>13</sup>CN<sup>-</sup> with an energy gap of 48 cm<sup>-1</sup> is  $102 \pm 10$  ps, about 2.8 times that from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> with a larger gap of 75 cm<sup>-1</sup>. These results show that the nonresonant energy transfer rates in solutions are strongly dependent on the energy gap. The vibrational-energy transfer between the nitrile stretches is faster with a smaller energy donor/acceptor gap.

Using the same procedure, the energy-transfer time constants in the other two solvents were also determined. In D<sub>2</sub>O solution, the energy-transfer time  $(1/k_{\rm CN}\rightarrow^{13}{\rm CN})$  from SCN<sup>-</sup> to S<sup>13</sup>CN<sup>-</sup> is 46 ± 7 ps, and that from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> is 115 ± 15 ps.<sup>28</sup> In DMF solution, the energy-transfer time  $(1/k_{\rm CN}\rightarrow^{13}{\rm C}^{15}{\rm N})$  from S<sup>13</sup>CN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> with an energy gap of 27 cm<sup>-1</sup> is 225 ± 20 ps. (Data and calculations are in the Supporting Information.) The energy-transfer time  $(1/k_{\rm CN}\rightarrow^{13}{\rm CN})$  from SCN<sup>-</sup> to S<sup>13</sup>CN<sup>-</sup> with a larger gap of 48 cm<sup>-1</sup> is 570 ± 50 ps, and that  $(k_{\rm CN}\rightarrow^{13}{\rm C}^{15}{\rm N})$  from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> with the largest gap of 75 cm<sup>-1</sup> is 1150 ± 100 ps.<sup>7</sup> As in the formamide solutions, the energy transfers are also slower with a larger energy gap in the D<sub>2</sub>O and DMF solutions.

**3.3.** Phonon Compensation with Instantaneous Normal Modes Cannot Describe Energy-Gap-Dependent Experiments. As discussed in the Introduction, one phonon compensation mechanisms are frequently used to describe nonresonant vibrational-energy transfers with gaps less than or close to the thermal energy.<sup>2,4,29,30</sup> The energy gap between the initial state (energy donor) and the final state(s) (energy acceptor) is believed to be compensated by the energy of low-frequency modes of the system during nonradiative transfer processes. In liquids, the low-frequency modes are composed of instantaneous normal modes, <sup>12,31–33</sup> the quanta

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Figure 4. (A,B) Two-dimensional IR spectra of (A) a 1:1 KSCN/KS<sup>13</sup>C<sup>15</sup>N formamide solution and (B) a 1:1 KSCN/KS<sup>13</sup>CN formamide solution with a 1:4 salt/solvent molar ratio at three waiting times. The maximum intensity in each plot is normalized to be 1. (C-F) Waiting-time-dependent intensities of (C,D) peaks 2, 3, 6, and 7 in panel A and (E,F) peaks 2, 4, 6, and 8 in panel B. Dots are experimental data, and curves are calculations based on the energy-exchange kinetic model.

of which are usually referred to as phonons, because the role played by instantaneous normal modes is believed to be analogous to that of the well-defined acoustic and optical phonon modes in crystals.<sup>4</sup> In vibrational relaxation theories, first-order perturbation theory with the first-order coupling matrix (eq 1) is typically employed to estimate the vibrationalenergy-transfer rate based on the Fermi golden rule.<sup>4,29</sup>

To use eq 1 to predict the energy-gap dependences of the vibrational-energy transfers among the nitrile stretches, let us analyze each of its parameters. The first parameter,  $V_{DA}$ , is the donor/acceptor (D/A) coupling strength, which is determined by the transition dipole interactions<sup>7</sup> and is therefore independent of the energy gap for potassium thiocyanate systems, as discussed above. The second parameter,  $V'_{s-b}$ , is the

system—bath coupling, which can be energy-gap-dependent. However, its independence of the energy gap is usually assumed.<sup>4</sup> This assumption is reasonable for small energy gaps with relatively large transition frequencies between the ground state and the excited state, because  $V'_{s-b}$  is determined by the difference between phonon modulations on the ground and first excited states.<sup>2,7</sup> In the systems studied in this work, the chemical properties of all of the nitrile stretches are essentially identical, and the largest first-excited-state energy difference between two nitrile stretches is only 75 cm<sup>-1</sup>, which is significantly smaller than the energy difference of ~2000 cm<sup>-1</sup> between the ground and first excited states. Therefore, it is reasonable to assume that  $V'_{s-b}$  is independent of the energy gap for potassium thiocyanate systems. The third parameter,  $ho_{\Delta E_{\mathrm{DA}'}}$  is the phonon density of the bath at the energy gap  $\Delta E_{\text{DA}}$ , which is energy-gap-dependent, as displayed in Figure 3. If the instantaneous normal modes are taken to be  $ho_{\Delta E_{
m DA}}$  as suggested in the literature, <sup>4</sup> the ratio of  $\rho_{\Delta E_{\mathrm{DA}}}$  values (the sum of INMs in Figure 3 in the range of the peak fwhm) at different gaps is  $\rho_{27 \text{ cm}^{-1}} / \rho_{48 \text{ cm}^{-1}} / \rho_{75 \text{ cm}^{-1}} = 1.16:1.17:1$  for the DMF solutions,  $\rho_{48 \text{ cm}^{-1}}/\rho_{75 \text{ cm}^{-1}}$  = 0.88:1 for the formamide solutions, and  $\rho_{48 \text{ cm}^{-1}}/\rho_{75 \text{ cm}^{-1}} = 0.95:1$  for the D<sub>2</sub>O solutions. The last parameter, N, is also gap-dependent. For the emission processes with gaps of 27, 48, and 75 cm<sup>-1</sup>, the ratio of values of  $N = [\exp(|\Delta E_{DA}|/RT) - 1]^{-1} + 1$  is  $N(27 \text{ cm}^{-1})/N(48)$  $cm^{-1}$ /N(75  $cm^{-1}$ ) = 2.5:1.5:1. Summarizing the above discussion, eq 1 predicts that, for the DMF solutions, the energy-gap dependence of the vibrational-energy-transfer rate constants is  $k_{13}_{CN \rightarrow 13} c_{15} (27 \text{ cm}^{-1}) / k_{CN \rightarrow 13} c_N (48 \text{ cm}^{$  $k_{\text{CN} \rightarrow {}^{13}\text{C}^{15}\text{N}}(75 \text{ cm}^{-1}) = 2.9:1.8:1$ . For the formamide solutions, the predicted gap dependence is  $k_{\rm CN\rightarrow {}^{13}CN}(48 \ {\rm cm}^{-1})/$  $k_{\text{CN}\rightarrow^{13}\text{C}^{15}\text{N}}(75 \text{ cm}^{-1}) = 1.3:1$ . For D<sub>2</sub>O solutions, the prediction is  $k_{\text{CN}\to^{13}\text{CN}}(48 \text{ cm}^{-1})/k_{\text{CN}\to^{13}\text{C}^{15}\text{N}}(75 \text{ cm}^{-1}) = 1.4:1.$ 

As introduced above, the experimental energy-gap dependences are  $k_{^{13}CN \rightarrow ^{13}C_{}^{15}N}(27 \text{ cm}^{-1})/k_{CN \rightarrow ^{13}CN}(48 \text{ cm}^{-1})/k_{CN \rightarrow ^{13}CN}(48 \text{ cm}^{-1})/k_{CN \rightarrow ^{13}CN}(48 \text{ cm}^{-1}) = 5.0:2.1:1$  in the DMF solutions,  $k_{CN \rightarrow ^{13}CN}(48 \text{ cm}^{-1})/k_{CN \rightarrow ^{13}CN}(75 \text{ cm}^{-1}) = 2.8:1$  in the formamide solutions, and  $k_{CN \rightarrow ^{13}CN}(48 \text{ cm}^{-1})/k_{CN \rightarrow ^{13}CN}(75 \text{ cm}^{-1}) = 2.5:1$  in the D<sub>2</sub>O solutions. These experimental results are almost 100% off from the predictions of eq 1.

Using a similar procedure to analyze the parameters of eq 2, we can also apply eq 2 to predict the energy-gap dependences in the three solvents. In the DMF solutions, eq 2 predicts  $k_{^{13}CN} \rightarrow {}^{13}C^{^{15}N}(27 \text{ cm}^{-1})/k_{CN} \rightarrow {}^{13}CN}(48 \text{ cm}^{-1})/k_{CN} \rightarrow {}^{13}CN}(75 \text{ cm}^{-1}) = 2.2.3:4.4:1$ . In the formamide solutions, eq 2 predicts  $k_{CN} \rightarrow {}^{13}CN}(48 \text{ cm}^{-1})/k_{CN} \rightarrow {}^{13}CN}(48 \text{ cm}^{-1}) = 3.2:1$ . The prediction for the D<sub>2</sub>O solutions is  $k_{CN} \rightarrow {}^{13}CN}(48 \text{ cm}^{-1})/k_{CN} \rightarrow {}^{13}CN}(75 \text{ cm}^{-1}) = 3.4:1$ . The predictions for the D<sub>2</sub>O and formamide solutions are somewhat close to the experimental results, but the prediction for the DMF solutions is very different from the experimental result.

Summarizing the above discussion, one can see that the predictions of either eq 1 or eq 2 cannot describe all of the experimental results.

3.4. Dephasing Mechanism Can Describe Energy-Gap-Dependent Experiments. Our previous studies suggested that the noncoherent  $(\tau^{-1} > V)$  resonant and nonresonant vibrational-energy transfers in liquids can be quantitatively described by the energy-transfer equation of the dephasing mechanism (eq 3).<sup>7,8</sup> In eq 3, to describe energygap-dependent experiments, there are only two unknown parameters: the dephasing line width  $\tau^{-1}$  and the D/A coupling strength V.  $\tau^{-1}$  must not be larger than the sum of the Lorenzian line widths of the donor and acceptor.<sup>7</sup> Both parameters are energy-gap-independent. Based on this information and the fact that  $\tau^{-1}$  is smaller than the energy gaps in the three solvents, the term  $(\Delta \omega)^2 + 4V^2 + \tau^{-2}$  in eq 3 can be approximated as  $(\Delta \omega)^2$ , and eq 3 predicts that the energy-gap dependence for the vibrational-energy transfers among the nitrile stretches is  $k_{13}_{CN \rightarrow 13} k_{13}^{15} (27 \text{ cm}^{-1})/$  $k_{\rm CN\rightarrow {}^{13}CN}(48 \text{ cm}^{-1})/k_{\rm CN\rightarrow {}^{13}C^{15}N}(75 \text{ cm}^{-1}) = 6.9:2.3:1.$  This predicted gap dependence is close to the energy-gap-dependent experimental results in all three solvents obtained in this work. The predicted  $k_{13}_{CN\rightarrow 13}C^{15}_{N}(27 \text{ cm}^{-1})$  value (6.9) is slightly larger than the measured one (5.0), because  $4V^2 + \tau^{-2}$ , which is assumed to be very small and ignored in the prediction, is

actually not much smaller than  $(\Delta \omega)^2$ . If  $4V^2 + \tau^{-2}$  is added into consideration, the predicted  $k^{_{13}}C_{N \rightarrow ^{13}C_{N}}(27 \text{ cm}^{-1})$  value is 5.6, which is very close to the measured value.

The above semiquantitative estimation based on eq 3 without tuning any parameters can already describe all three energy-transfer systems simultaneously very well. In fact, all of the energy-gap-dependent experimental results can be quantitatively reproduced by eq 3. The two unknown parameters ( $\tau^{-1}$  and V) can be obtained by solving eq 3 with energy-transfer results for at least two different energy gaps. For the DMF solutions, substituting the four energy-transfer time constants 49.4 ps ( $\Delta \omega = 0$ ),<sup>7</sup> 225 ps ( $\Delta \omega = 27 \text{ cm}^{-1}$ ), 570 ps  $(\Delta \omega = 48 \text{ cm}^{-1})$ , and 1150 ps  $(\Delta \omega = 75 \text{ cm}^{-1})$  (none of the energy-transfer time constants were normalized for the fewpercent concentration fluctuations, as the overall uncertainty was estimated to be  $\sim 10\%$ ) into eq 3, we obtain the coupling strength V = 1.25 cm<sup>-1</sup> and the dephasing width  $\tau^{-1} = 14$  cm<sup>-1</sup> with the calculated time constants 49 ps ( $\Delta \omega = 0$ ), 211 ps ( $\Delta \omega$ = 27 cm<sup>-1</sup>), 542 ps ( $\Delta \omega$  = 48 cm<sup>-1</sup>), and 1191 ps ( $\Delta \omega$  = 75  $cm^{-1}$ ). Within experimental uncertainty (~10%), the calculated energy-transfer times for all four different gaps are identical to the measured values. For the D<sub>2</sub>O solutions, substituting the three energy-transfer time constants 6 ps  $(\Delta \omega = 0)^7$  46 ps  $(\Delta \omega = 48 \text{ cm}^{-1})$ , and 115 ps  $(\Delta \omega = 75 \text{ cm}^{-1})$  into eq 3, we obtain the coupling strength  $V = 4.1 \text{ cm}^{-1}$  and the dephasing width  $\tau^{-1} = 15$  cm<sup>-1</sup> with the calculated time constants 6.1 ps  $(\Delta \omega = 0)$ , 49 ps  $(\Delta \omega = 48 \text{ cm}^{-1})$ , and 105 ps  $(\Delta \omega = 75 \text{ cm}^{-1})$ <sup>1</sup>). Again, within experimental uncertainty (~10%), the calculated energy-transfer times for all three gaps are identical to the measured values. The experimental results and predictions for the energy transfers in the two solvents are plotted in Figure 5.



Figure 5. Energy-gap-dependent energy-transfer (ET) times in DMF and  $D_2O$  solutions determined by experimental results (symbols) and predicted by the dephasing energy-transfer equation (eq 3) (lines).

Similarly, for the formamide solutions, substituting the two energy-transfer time constants 102 ps ( $\Delta \omega = 48 \text{ cm}^{-1}$ ) and 290 ps ( $\Delta \omega = 75 \text{ cm}^{-1}$ ) into eq 3, we obtain the coupling strength  $V = 2.6 \text{ cm}^{-1}$  and the dephasing width  $\tau^{-1} = 14 \text{ cm}^{-1}$  with the calculated time constants 127 ps ( $\Delta \omega = 48 \text{ cm}^{-1}$ ) and 277 ps ( $\Delta \omega = 75 \text{ cm}^{-1}$ ). The predictions are again very close to the experimental results.

In summary, the energy-gap-dependent vibrational-energy transfers among the nitrile stretches in the three solvents cannot be described simultaneously by the phonon compensation mechanisms (eqs 1 and 2), but all of them can be quantitatively reproduced by the dephasing mechanism (eq 3). The experimental results and predictions are listed in Table 2.

#### Table 2. Experimental and Predicted Energy-Gap Dependences

|                                                                                                                                                                          |             | predictions |            |           |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|-------------|------------|-----------|
|                                                                                                                                                                          | experiments | eq 1        | eq 2       | eq 3      |
| $k_{{}^{13}CN \rightarrow {}^{13}C}(27 \text{ cm}^{-1})/k_{CN \rightarrow {}^{13}CN}(48 \text{ cm}^{-1})/k_{CN \rightarrow {}^{13}C}(75 \text{ cm}^{-1}) \text{ in DMF}$ | 5.0:2.1:1   | 2.9:1.8:1   | 22.3:4.4:1 | 5.6:2.2:1 |
| $k_{\rm CN \rightarrow {}^{13}CN}(48 \text{ cm}^{-1})/k_{\rm CN \rightarrow {}^{13}C} (75 \text{ cm}^{-1}) \text{ in } D_2O$                                             | 2.5:1       | 1.4:1       | 3.4:1      | 2.2:1     |
| $k_{\rm CN \to {}^{13}CN}(48 \text{ cm}^{-1})/k_{\rm CN \to {}^{13}C^{15}N}(75 \text{ cm}^{-1})$ in formamide                                                            | 2.8:1       | 1.3:1       | 3.2:1      | 2.2:1     |

3.5. Fast Molecular Motions in Liquids Diminish Phonon Compensation. One possible reason for the inability of the phonon compensation mechanisms described by eqs 1 and 2 to describe the energy-gap-dependent vibrational-energytransfer experiments in solution is that the assumptions of the system-bath coupling being independent of the gap and all of the instantaneous normal modes participating equally in the compensation might be invalid. However, this possibility is very difficult to test experimentally, because, to the best of our knowledge, no existing experimental tools are able to quantitatively determine the system-bath coupling strength or the phonon densities involved in the energy compensation process.

In addition to the above possibility, we believe that there is an intrinsic reason for the failure of the phonon compensation mechanisms to work for the nonresonant energy transfers studied in this work if the instantaneous normal modes are taken to be the phonons. The essential reason is that the very fast molecular motions in the liquids randomize the modulations on the energy donor and acceptor by the phonons and diminish the collective compensation effect of phonons for the much slower energy-transfer process. In the following discussion, a simple derivation of the one-phonon compensation process with the second-order coupling matrix is provided to illustrate this point.

The energy-transfer rate from the initial state  $|i\rangle$  to the final state  $|f\rangle$  of the energy-transfer process is proportional to the transition probability

$$P(i \to f) = |c_f^{(1)}(t) + c_f^{(2)}(t) + \dots|^2$$
(4)

where

$$c_f^{(1)}(t) = \left(\frac{-\mathrm{i}}{\hbar}\right) \int_{t_0}^t \mathrm{e}^{\mathrm{i}\omega_j t'} \langle f | H'(t') | i \rangle \,\mathrm{d}t'$$
(5)

$$c_{f}^{(2)}(t) = \left(\frac{-\mathrm{i}}{\hbar}\right)^{2} \sum_{m} \int_{t_{0}}^{t} \mathrm{d}t' \int_{t_{0}}^{t'} \mathrm{d}t'' \, \mathrm{e}^{\mathrm{i}\omega_{jm}t'} \langle f|H'(t')|m\rangle$$
$$\mathrm{e}^{\mathrm{i}\omega_{mi}t''} \langle m|H'(t'')|i\rangle \tag{6}$$

 $\omega_{fi} = (E_f - E_i)/\hbar, \ \omega_{fm} = (E_f - E_m)/\hbar, \ \omega_{mi} = (E_m - E_i)/\hbar, \ \text{and} \ |$ m denotes all possible intermediate states.

The Hamiltonian H' consists of the direct interaction between donor and acceptor,  $H_{\rm DA}$ , and the couplings between the phonons and the system,  $H_{ph}(D)$  (with the donor) and  $H_{\rm ph}(A)$  (with the acceptor)

$$H' = H_{\rm DA} + H_{\rm ph}(\rm D) + H_{\rm ph}(\rm A)$$
 (7)

The initial state is

$$|i\rangle = |\mathsf{D}^*, \mathsf{A}, n_{\mathbf{q}}\rangle \tag{8}$$

where the donor D is in its first excited state D\*, the acceptor A is in the ground state A, and the phonon state is  $n_{g}$ . The final state is

$$\begin{array}{c} 3.0.2.1.1 & 2.5.1.6.1 & 2.2.5.4.1 & 3.0.2.2.1 \\ \hline 2.5.1 & 1.4:1 & 3.4:1 & 2.2:1 \\ \hline 2.8:1 & 1.3:1 & 3.2:1 & 2.2:1 \\ \hline |f\rangle = |D, A^*, n_{q} \pm 1\rangle \end{array} \tag{9}$$

where the donor D is in the ground state D, the acceptor A is in its first excited state A\*, and the phonon state is  $n_q \pm 1$ . The initial and final states have the same energy  $E_i$ . The energy gap between the donor and acceptor,  $\Delta E = E_D - E_A$ , is compensated by one phonon, and the upper and lower signs of  $n_{\rm q} \pm 1$  designate phonon emission if  $\Delta E > 0$  and absorption if  $\Delta E < 0$ , respectively. The two possible intermediate states<sup>2</sup> are

$$|m_1\rangle = |\mathrm{D}^*, \,\mathrm{A}, \,n_\mathbf{q} \pm 1\rangle \tag{10}$$

$$|m_2\rangle = |\mathbf{D}, \mathbf{A}^*, n_{\mathbf{q}}\rangle \tag{11}$$

with energies of  $E_i + \Delta E$  and  $E_i - \Delta E_i$ , respectively. **q** denotes the wave vector of the phonon whose energy is  $\hbar\omega(\mathbf{q}) = |\Delta E|$ .

The first-order coupling matrix element  $\langle f|H'(t')|i\rangle$  is negligibly small.7 We define the following terms for the second-order coupling matrix

$$\langle \mathbf{D}, \mathbf{A}^* | H_{\mathbf{D}\mathbf{A}} | \mathbf{D}^*, \mathbf{A} \rangle = V$$

$$\langle \mathbf{D}, n_{\mathbf{q}} \pm 1 | H_{\mathrm{ph}}(\mathbf{D}) | \mathbf{D}, n_{\mathbf{q}} \rangle = g_{\mathbf{D}}(s, q) \langle n_{\mathbf{q}} \pm 1 | (b_{s,q}^{\dagger} + b_{s,-q}) | n_{\mathbf{q}} \rangle$$

$$\exp[\mp \mathbf{i} \mathbf{q} \cdot \mathbf{r}_{\mathbf{D}}) \exp[i\varphi(t)]$$

$$\begin{split} \langle \mathbf{A}, \, n_{\mathbf{q}} \, \pm \, 1 | H_{\mathrm{ph}}(\mathbf{A}) | \mathbf{A}, \, n_{\mathbf{q}} \rangle &= g_{\mathbf{A}}(s, \, q) \, \langle n_{\mathbf{q}} \, \pm \, 1 | (b_{s,q}^{\dagger} \, + \, b_{s,-q}) | n_{\mathbf{q}} \rangle \\ &\exp[\mp \mathbf{i} \mathbf{q} \cdot \mathbf{r}_{\mathbf{A}}) \exp[\mathrm{i} \varphi(t)] \end{split}$$

$$\begin{aligned} \langle \mathbf{D}^*, \, n_{\mathbf{q}} \pm 1 | H_{\mathrm{ph}}(\mathbf{D}) | \mathbf{D}^*, \, n_{\mathbf{q}} \rangle &= e_{\mathrm{D}}(s, \, q) \, \langle n_{\mathbf{q}} \pm 1 | (b_{s,q}^{\dagger} + b_{s,-q}) | n_{\mathbf{q}} \rangle \\ &\exp(\mp \mathbf{i} \mathbf{q} \cdot \mathbf{r}_{\mathrm{D}}) \exp[\mathbf{i} \varphi(t)] \end{aligned}$$

$$\langle \mathbf{A}^*, \, n_{\mathbf{q}} \pm 1 | H_{\text{ph}}(\mathbf{D}) | \mathbf{A}^*, \, n_{\mathbf{q}} \rangle = e_{\mathbf{A}}(s, q) \langle n_{\mathbf{q}} \pm 1 | (b_{s,q}^{\dagger} + b_{s,-q}) | n_{\mathbf{q}} \rangle$$

$$\exp[\mp \mathbf{i} \mathbf{q} \cdot \mathbf{r}_{\mathbf{A}}) \exp[i\varphi(t)]$$

where  $g_i(s,q)$  and  $e_i(s,q)$  (*i* = D, A) denote the coupling between the phonon of wave vector  $\mathbf{q}$  (branch s) and the ground state and first excited state of *i*, respectively.  $b_{s,q}^{\dagger}$ ,  $b_{s,-q}$  are the phonon creation and annihilation operators, respectively.  $\mathbf{r}_{\mathrm{D}}$ and  $\mathbf{r}_A$  are the position vectors of the donor and acceptor, respectively, and  $\exp[i\varphi(t)]$  denotes the phase fluctuation caused by the change of  $\mathbf{r}_{\rm D}$  or  $\mathbf{r}_{\rm A}$  because of molecular motions. Therefore, the second-order coupling matrix elements are

$$\langle f|H'(t')|m_1\rangle = \langle D, A^*|H_{DA}|D^*, A\rangle = V$$

$$\begin{split} \langle m_{1} | H'(t'') | i \rangle &= \langle \mathbf{D}^{*}, n_{\mathbf{q}} \pm 1 | H_{\mathrm{ph}}(\mathbf{D})(t'') | \mathbf{D}^{*}, n_{\mathbf{q}} \rangle \\ &+ \langle \mathbf{A}, n_{\mathbf{q}} \pm 1 | H_{\mathrm{ph}}(\mathbf{A})(t'') | \mathbf{A}, n_{\mathbf{q}} \rangle \\ &= \langle n_{\mathbf{q}} \pm 1 | (b_{s,q}^{\dagger} + b_{s,-q}) | n_{\mathbf{q}} \rangle [e_{\mathrm{D}}(s, q) \exp(\mp \mathbf{i} \mathbf{q} \cdot \mathbf{r}_{\mathrm{D}}) \\ &+ g_{\mathrm{A}}(s, q) \exp(\mp \mathbf{i} \mathbf{q} \cdot \mathbf{r}_{\mathrm{A}})] \exp[\mathbf{i} \varphi(t'')] \end{split}$$

$$\langle f|H'(t')|m_2 \rangle = \langle \mathbf{D}, n_{\mathbf{q}} \pm 1|H_{\mathrm{ph}}(\mathbf{D})(t')|\mathbf{D}, n_{\mathbf{q}} \rangle$$

$$+ \langle \mathbf{A}^*, n_{\mathbf{q}} \pm 1|H_{\mathrm{ph}}(\mathbf{A})(t')|\mathbf{A}^*, n_{\mathbf{q}} \rangle$$

$$= \langle n_{\mathbf{q}} \pm 1|(b_{s,q}^{\dagger} + b_{s,-q})|n_{\mathbf{q}} \rangle [g_{\mathbf{D}}(s, q) \exp(\mp \mathbf{i}\mathbf{q} \cdot \mathbf{r}_{\mathbf{D}})$$

$$+ e_{\mathbf{A}}(s, q) \exp(\mp \mathbf{i}\mathbf{q} \cdot \mathbf{r}_{\mathbf{A}})] \exp[\mathbf{i}\varphi(t')]$$

$$\langle m_2 | H'(t'') | i \rangle = \langle \mathbf{D}, \mathbf{A}^* | H_{\mathbf{D}\mathbf{A}} | \mathbf{D}^*, \mathbf{A} \rangle = V$$

The time-dependent terms in the integral in eq 6 can be written as

$$\begin{split} &\int_{0}^{t} dt' \int_{0}^{t'} dt'' e^{i\omega_{jm_{1}}t'} e^{i\omega_{m_{1}}t''} e^{i\varphi(t'')} \\ &= \int_{0}^{t} dt'' \int_{t''}^{t} dt' e^{i\omega_{jm_{1}}t'} e^{i\omega_{m_{1}}t''} e^{i\varphi(t'')} \\ &= \int_{0}^{t} dt'' e^{i\omega_{m_{1}}t''} e^{i\varphi(t'')} \frac{e^{i\omega_{jm_{1}}t} - e^{i\omega_{jm_{1}}t''}}{i\omega_{jm_{1}}} \\ &= \int_{0}^{t} dt'' e^{i\varphi(t'')} \frac{e^{i\omega_{m_{1}}t''} e^{i\omega_{jm_{1}}t} - e^{i\omega_{j}t''}}{i\omega_{jm_{1}}} \\ &\approx -\frac{1}{i\omega_{jm_{1}}} \int_{0}^{t} dt'' e^{i\varphi(t'')} e^{i\omega_{j}t''} \\ &= -\frac{1}{i\omega_{jm_{1}}} \int_{0}^{t} dt' e^{i\varphi(t')} e^{i\omega_{j}t'} \end{split}$$
(12)

and

$$\int_{0}^{t} dt' \int_{0}^{t'} dt'' e^{i\omega_{jm_{2}}t'} e^{i\omega_{m_{2}i}t''} e^{i\varphi(t')}$$

$$= \int_{0}^{t} dt' e^{i\omega_{jm_{2}}t'} e^{i\varphi(t')} \frac{e^{i\omega_{m_{2}i}t'} - 1}{i\omega_{m_{2}i}}$$

$$= \int_{0}^{t} dt' e^{i\varphi(t')} \frac{e^{i\omega_{ji}t'} - e^{i\omega_{jm_{2}}t'}}{i\omega_{m_{2}i}} \approx \frac{1}{i\omega_{m_{2}i}} \int_{0}^{t} dt' e^{i\varphi(t')} e^{i\omega_{ji}t'}$$
(13)

where  $\omega_{fm_1} \approx \omega_{m_2i} = -\Delta E/\hbar$ ,  $\omega_{fm_2} \approx \omega_{m_ii} = -\Delta E/\hbar$ , and  $\omega_{if} = \omega_{fi} \approx 0$ . Because the exponential terms that contain  $\omega_{nm_k}$  (n = i, f; k = 1, 2) in eqs 12 and 13 give rise to a rapid oscillation (compared to the terms that contain  $\omega_{if}$ ), they do not contribute to the transition probability that grows with *t*. Equation 6 can now be rewritten as

$$c_{f}^{(2)}(t) = \left(\frac{-\mathrm{i}}{\hbar}\right)^{2} \sum_{m} \int_{t_{0}}^{t} \mathrm{d}t' \int_{t_{0}}^{t'} \mathrm{d}t'' \, \mathrm{e}^{\mathrm{i}\omega_{fm}t'} \langle f|H'(t')|m\rangle \mathrm{e}^{\mathrm{i}\omega_{mi}t''} \langle m|H'(t'')|i\rangle = \left(\frac{-\mathrm{i}}{\hbar}\right) \frac{V}{\Delta E} \langle n_{\mathbf{q}} \pm 1|(b_{s,q}^{\dagger} + b_{s,-q})|n_{\mathbf{q}}\rangle V_{\mathrm{ph}}(s, q) \exp(\mp \mathrm{i}\mathbf{q}\cdot\mathbf{r}_{\mathrm{A}})[\exp(\pm \mathrm{i}\mathbf{q}\cdot\mathbf{r}) - 1] \int_{0}^{t} \mathrm{d}t' \, \mathrm{e}^{\mathrm{i}\varphi(t')} \mathrm{e}^{\mathrm{i}\omega_{fi}t'} = \left(\frac{-\mathrm{i}}{\hbar}\right) W_{fi}(q) \int_{0}^{t} \mathrm{d}t' \, \mathrm{e}^{\mathrm{i}\varphi(t')} \mathrm{e}^{\mathrm{i}\omega_{fi}t'}$$
(14)

where  $W_{fi}(q) = (V/\Delta E)\langle n_{\mathbf{q}} \pm 1|b_{s,q}^{\dagger} + b_{s,-q}|n_{\mathbf{q}}\rangle V_{\text{ph}}(s,q) \exp(i\mathbf{q}\cdot\mathbf{r}_{A}) [\exp(\pm i\mathbf{q}\cdot\mathbf{r}) - 1]$  with  $V_{\text{ph}}(s,q) = g_{D}(s,q) - e_{D}(s,q) = g_{A}(s,q) - e_{A}(s,q)$  and  $\mathbf{r} = \mathbf{r}_{A} - \mathbf{r}_{D}$  is the same as the coupling matrix with a constant phase that was derived previously.<sup>7</sup> As a result, the transition probability is

$$P(i \to f) = |c_{f}^{(2)}(t)|^{2} = \frac{1}{\hbar^{2}} |W_{fi}(q)|^{2} |\int_{0}^{t} dt' e^{i\varphi(t')} e^{i\omega_{fi}t'}|^{2}$$
$$= \frac{1}{\hbar^{2}} |W_{fi}(q)|^{2} |\sum_{i=1}^{N} e^{i\varphi_{i}} \int_{t_{i}}^{t_{i}+\Delta t_{i}} dt' e^{i\omega_{fi}t'}|^{2}$$
(15)

Here, we let  $e^{i\varphi(t')} = e^{i\varphi_i}$  when  $t_i \leq t' < t_i + \Delta t_i$ . As one can see from the definition of  $W_{fi}(q)$ , the amplitude, and therefore the energy-transfer rate from *i* to *f*, is determined by the difference  $([\exp(\pm i\mathbf{q}\cdot\mathbf{r}) - 1])$  in the phonon modulations on the donor and acceptor. The fast molecular motions in liquids, for example, the donor and acceptor switching positions, can randomize the modulations. The randomization is reflected by the term  $|\sum_{i=1}^{N} e^{i\varphi_i} \int_{t_i}^{t_i + \Delta t_i} dt' e^{i\omega_j t'}|^2$  in eq 15. At time  $t_i$  the phase changes to  $\varphi_i$  and then remains constant for a time duration of  $\Delta t_i$ . When  $\omega_{fi} = (E_f - E_i)/\hbar \approx 0$  (conversation of energy),  $\int_{t_i}^{t_i + \Delta t_i} dt' e^{i\omega_j t'} \approx \Delta t_i$ , and eq 15 is similar to a two-dimensional random-walk problem.

For  $\omega_{fi} = (E_f - E_i)/\hbar = 0$ , if  $\Delta t_i = t/Q$  (assuming discrete molecular motions), we have

$$\begin{aligned} \left|\sum_{i=1}^{Q} \int_{t_{i}}^{t_{i}+\Delta t_{i}} \mathrm{d}t' \, \mathrm{e}^{\mathrm{i}\varphi_{i}} \mathrm{e}^{\mathrm{i}\omega_{j}t'}\right|^{2} &\approx \left|\sum_{i=1}^{Q} \mathrm{e}^{\mathrm{i}\varphi_{i}} \Delta t_{i}\right|^{2} \approx \left|\frac{t}{Q} \sum_{i=1}^{Q} \mathrm{e}^{\mathrm{i}\varphi_{i}}\right|^{2} \\ &= \left(\frac{t}{Q}\right)^{2} \sum_{i=1}^{Q} \mathrm{e}^{\mathrm{i}\varphi_{i}} \sum_{j=1}^{Q} \mathrm{e}^{-\mathrm{i}\varphi_{j}} = \left(\frac{t}{Q}\right)^{2} \sum_{i=1}^{Q} \sum_{j=1}^{Q} \mathrm{e}^{\mathrm{i}(\varphi_{i}-\varphi_{j})} \\ &= \left(\frac{t}{Q}\right)^{2} (Q + \sum_{i,j=1, i\neq j}^{Q} \mathrm{e}^{\mathrm{i}(\varphi_{i}-\varphi_{j})}) \end{aligned}$$
(16)

After averaging all possible phases, we obtain

$$\langle |\sum_{i=1}^{Q} \int_{t_{i}}^{t_{i}+\Delta t_{i}} dt' e^{i\varphi_{i}} e^{i\omega_{j}t'}|^{2} \rangle$$

$$\approx \left(\frac{t}{Q}\right)^{2} (Q + \langle \sum_{i,j=1,i\neq j}^{Q} e^{i(\varphi_{i}-\varphi_{j})} \rangle) = \frac{t^{2}}{Q}$$

$$(17)$$

For the last step, considering that  $\varphi_i$  and  $\varphi_j$  are two uncorrelated random variables, the difference between them is also a random variable. After averaging the term of summation, all of the positive and negative values cancel each other out, yielding an expectation value of 0.

If the phase  $\varphi(t)$  is a constant (no molecular motions), then the term in eq 15 is

$$|\int_{0}^{t} dt' e^{i\varphi(t')} e^{i\omega_{ji}t'}|^{2} = |\int_{0}^{t} dt' e^{i\omega_{ji}t'}|^{2} \approx t^{2}$$
(18)

Comparing eqs 17 and 18, one can see that, with the consideration of the random phase of the coupling matrix, the energy-transfer rate, which is proportional to the transition probability  $P(i \rightarrow f)$ , is reduced to 1/Q of that with a constant phase.

Based on eqs 17 and 18, the nonresonant energy-transfer times among the nitrile stretches can be estimated. If we take 1000 m/s as the speed of molecular motions in the liquids (the speed of sound in water at room temperature is about 1450 m/s), it takes 100 fs for the molecules to move 1 Å. The D/A distance in potassium thiocyanate solutions is about 4 Å. Therefore, the long limit of the time constant of phonon-modulation randomization is about 1/e of the time needed to change one cycle, which is 294 fs  $\{100 \text{ fs} \times [(2 \times 4)/(1 \times e)]\}$ .

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(The randomization of the spatial distribution of INMs can further facilitate phonon-modulation randomization.) In addition, the rate of nonresonant energy transfer compensated by phonons cannot exceed that of resonant energy transfer, because nonresonant energy transfer is a process that is one order higher than the resonant energy-transfer process. Typically, it is at least about 1 order of magnitude slower. To estimate the fast limit of the phonon-compensated energytransfer rate with phase randomization by molecular motions, we assume that phonon compensation without phase randomization can be very efficient, up to 30% of the resonant transfer rate. This value is close to the efficiency of BBO crystal doubling or splitting photons. In D<sub>2</sub>O solutions, the resonant energy-transfer time among the nitrile stretches is 6 ps. According to eqs 17 and 18, the fast limit of the time constant of the nonresonant energy transfer compensated by the instantaneous normal modes is 408 ps {= 6 ps  $\times [6/(0.3 \times$ 0.294)]}. In reality, the phonon compensation efficiency should be lower than 30%, and the nonresonant energy transfer between nitrile stretches in D<sub>2</sub>O solution must be much slower than 408 ps. This time constant is much longer than the measured constants of 46 and 115 ps for the two nonresonant energy transfers with gaps of 48 and 75 cm<sup>-1</sup>, respectively, indicating that the phonon (instantaneous normal mode) compensation plays a very minor role in the experimentally measured nonresonant vibrational-energy transfers. This explains well why the phonon compensation mechanisms cannot describe the experimental results. Similarly, for the DMF solutions, the fastest limit of the time constant of nonresonant energy transfer compensated by the instantaneous normal modes is 27222 ps {=  $49ps \times [49/(0.3 \times 0.294)]$ }, which is significantly slower than the two measured nonresonant energy-transfer times (570 and 1150 ps).

Based on the above analyses, we can give a general estimation of the relative importance of the dephasing mechanism and the phonon compensation mechanism by the instantaneous normal modes for nonresonant vibrational-energy transfer in a liquid. If we one assume that the energy dephasing width is  $20 \text{ cm}^{-1}$  and the coupling strength is  $4 \text{ cm}^{-1}$ , which is larger than most intermolecular vibrational transition dipole couplings, according to eq 3, the resonant energy-transfer time for such a system at room temperature is 7.7 ps. Using the same procedure as discussed above, the fast limit of the energy-transfer time through the phonon compensation mechanism is estimated to be 672 ps. According to eq 3, the nonresonant energy transfer needs to have an energy gap larger than  $250 \text{ cm}^{-1}$  to be so slow. In other words, for nonresonant vibrational-energy transfer with a gap smaller than the thermal energy ( $\sim 200 \text{ cm}^{-1}$ ) at room temperature, the energy transfer is dominated by the dephasing mechanism. Because the vibrational parameters used in the estimation are typical and the estimated energy-transfer time is at the upper limit, we expect that the conclusion from the estimation that nonresonant vibrational-energy transfers with gaps smaller than the thermal energy in liquids should be dominated by the dephasing mechanism is general for most intermolecular vibrational-energy transfers.

Here, we want to emphasize that the reason for the inefficient phonon compensation by the instantaneous normal modes is the randomization of their modulations on the donor and acceptor. If the phonons are internal vibrational modes of the solvent, we expect that the randomization of the phonon modulations caused by molecular motions will be smaller because the donor and acceptor are always surrounded by solvent molecules regardless of how molecules are moving around in the liquids. Therefore, the energy transfers compensated by such solvent internal vibrational modes are expected to be more efficient than those compensated by the instantaneous normal modes, provided that other necessary conditions for energy transfers are identical. Similarly, if the phonons are internal modes of the donor or acceptor, the randomization effect caused by molecular motions will also be very small, because intramolecular coupling will make the coupling strengths of phonons to the donor and the acceptor very different and molecular motions should have little effect on such a difference. Certainly, we believe that this situation should be relatively rare because very few internal modes have frequencies lower than 200 cm<sup>-1</sup>.

The above derivation and discussion provide a rational explanation to address why the conventional intuitive picture used to justify the phonon mechanism, namely, that time scales do not matter,<sup>4</sup> is not sufficient to describe the phonon compensated energy transfers. Time scales do matter for the phonon compensation mechanisms. The intrinsic reason for this conclusion is that, as shown in eqs 14 and 15, the difference in phonon modulations on the donor and acceptor, which is represented by  $\mathbf{r} = \mathbf{r}_{A} - \mathbf{r}_{D}$  in the equations, must be nonzero for energy transfer to occur. If the energy transfer is much slower than the molecular motions, the fast molecular motions in liquids lead to very similar average  $\mathbf{r}_A$  and  $\mathbf{r}_D$  values, resulting in a very small r value and, therefore, a very low energy-transfer rate (eq 15). As discussed above, this turns out to be quite general for nonresonant vibrational-energy transfers in liquids. The pronounced phonon-compensation effect in crystalline samples where molecular motions are significantly slower than those in liquids presented in the following paragraph further supports the conclusion that time scales are important for phonon compensation.

In crystals, molecules cannot translate, and the randomization effect of phonon modulations by molecular motions is significantly smaller than in liquids. Therefore, in some crystals, the phonon compensation mechanisms can play a dominant role over the dephasing mechanism in nonresonant vibrationalenergy transfers, leading to inverted gap-dependent energy transfers.<sup>7</sup> Figure 6 illustrates such an example. Figure 6A,B displays the 2D IR spectra (only 0-1 transitions are plotted) of the 1:1 KSCN/KS<sup>13</sup>CN DMF 1:8 solution (with an energy gap of 48 cm<sup>-1</sup>) and the 1:1 KSCN/KS<sup>13</sup>C<sup>15</sup>N DMF 1:8 solution (with an energy gap of 75  $cm^{-1}$ ) at room temperature at a waiting time 50 ps. Because the energy transfers are governed by the dephasing mechanism, the energy transfer is slower with a larger gap, leading to energy-transfer cross-peaks 5 and 7 that are smaller with a larger gap (Figure 6B). On the contrary, in mixed crystals (Figure 6C,D), the phonon compensation mechanism dominates energy transfers.<sup>7</sup> The energy transfer is faster with a larger gap because the phonon density at a larger gap is higher (Figure 1H,I), leading to larger energy-transfer cross-peaks 5 and 7 (Figure 6D). The detailed energy-transfer kinetics in mixed potassium thiocyanate crystals were reported previously."

#### 4. CONCLUDING REMARKS

Energy-gap-dependent vibrational-energy transfers among the nitrile stretches of  $\rm KSCN/KS^{13}CN/KS^{13}C^{15}N$  in D<sub>2</sub>O, DMF, and formamide liquid solutions at room temperature were measured by the vibrational-energy-exchange method. The energy transfers were slower with a larger donor/acceptor

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Figure 6. (A,B) Two-dimensional IR spectra of (A) 1:1 KSCN/ $KS^{13}CN$  DMF solution (with an energy gap of 48 cm<sup>-1</sup>) and (B) 1:1 KSCN/ $KS^{13}C^{15}N$  DMF solution (with an energy gap of 75 cm<sup>-1</sup>) at room temperature at a waiting time 50 ps. (C,D) Two-dimensional IR spectra of (C) 1:1 KSCN/ $KS^{13}CN$  mixed crystal (with an energy gap of 48 cm<sup>-1</sup>) and (D) 1:1 KSCN/ $KS^{13}C^{15}N$  mixed crystal (with an energy gap of 75 cm<sup>-1</sup>) at a waiting time 150 ps at 80 K. In the figures, only the 0–1 transition signals are plotted.

energy gap, independent of the calculated instantaneous normal mode densities of the solutions or the terahertz absorption spectra of the solvent. The energy-gap dependences of the nonresonant energy transfers cannot be described by the popular phonon compensation mechanisms with the assumption that phonons are the instantaneous normal modes. Instead, the experimental energy-gap dependences can be quantitatively reproduced by the dephasing mechanism. A simple theoretical derivation shows that a critical reason for the observed nonresonant vibrational-energy transfers being independent of the instantaneous normal mode (INM) densities is that the molecular motions in liquids are too fast compared to the energy-transfer time. The fast molecular motions randomize the phonon modulations on the energy donor and acceptor, diminishing the phonon compensation efficiency for the energy transfer. Estimations based on theoretical derivations suggest that, for most nonresonant intermolecular vibrational-energy transfers in liquids with energy gaps smaller than the thermal energy, the dephasing mechanism dominates the energytransfer process, which can be quantitatively described by the dephasing energy-transfer equation (eq 3), unless the phonons compensating the energy transfer are some specific internal vibrational modes of either the solvent or the donor or acceptor that are strongly coupled to the energy-transfer system, which we believe to be relatively rare because very few internal modes have frequencies lower than 200 cm<sup>-1</sup>.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Additional information as noted in text. 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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# Supporting Information

# Nonresonant Energy Transfers Independent on the Phonon Densities in Polyatomic

Liquids

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## **Kinetic Models**

To analyze the nonresonant energy trasnfers in samples, we used the kinetic model we previously developed using KSCN/KS<sup>13</sup>C<sup>15</sup>N=1/1 formamide solution with a 1/4 salt molar ratio as an example (fig.2C&D):<sup>1,2</sup>

$$\underbrace{\overset{k_{S^{13}c^{15}N^-}}{\longleftarrow}}_{S^{cN^-}}[S^{13}C^{15}N^-]\underbrace{\overset{k_{S^{13}c^{15}N^-}\rightarrow S^{cN^-}}{\longleftarrow}}_{k_{S^{cN^-}}\rightarrow S^{13}c^{15}N^-}[S^{cN^-}]\overset{k_{S^{cN^-}}\rightarrow S^{13}c^{15}N^-}{\longleftarrow}$$

where  $[S^{13}C^{15}N^{-}]$  denotes the population of excited  $S^{13}C^{15}N^{-}$  anion, and  $[SCN^{-}]$  denotes the population of excited SCN<sup>-</sup> anion.  $k_{s^{13}c^{15}N^- \rightarrow scN^-}$  represents the energy transfer rate constant from  $S^{13}C^{15}N^{-}$  to  $SCN^{-}$  and  $k_{scN^{-} \rightarrow s^{13}c^{15}N^{-}}$  represents the transfer rate constant from SCN<sup>-</sup> to S<sup>13</sup>C<sup>15</sup>N<sup>-</sup>.  $k_{s^{13}c^{15}N^-}$  and  $k_{s^{cN^-}}$  are the vibrational lifetimes of S<sup>13</sup>C<sup>15</sup>N<sup>-</sup> and SCN<sup>-</sup>, respectively, which can be single or biexponetial dependent on the experiemental results.<sup>1,2</sup> In this work, both CN vibrational decays are observed to be bi-exponential. Vibrational bi-exponential decay is frequently observed for modes in the range of 2000~2300 cm<sup>-1</sup>.<sup>1-4</sup> It has been attributed to the fast vibrational equilibrium between the bright mode and one coupled dark mode.<sup>3</sup> Here, we adopted the method we developed for bi-exponential decays to analyze the kinetics.<sup>1-3</sup> We separate each CN stretch into two subgroups. The weighing factor of each subgroup is determined by the prefactors of the bi-exponential. Each subgroup has a single-exponential-decay lifetime time. Each subgroup can exchange energy with other CN stretches, but the subgroups can't exchange energy with each other (this follows the assumed physical picture of bi-exponential: the sub-components can be considered as independent species). In the model, the effects of dynamics: spectral diffusions, vibrational decays and vibrational exchanges within each species are simply treated as apparent vibrational decays as experimentally measured.

According to the scheme, we have kinetic equations:

$$\begin{cases} \frac{d[SCN^{-}]}{dt} = -k_{SCN^{-}}[SCN^{-}] + k_{S^{13}C^{15}N^{-} \to SCN^{-}}[S^{13}C^{15}N^{-}] - k_{SCN^{-} \to S^{13}C^{15}N^{-}}[SCN^{-}] \\ \frac{d[S^{13}C^{15}N^{-}]}{dt} = -k_{S^{13}C^{15}N^{-} \to SCN^{-}}[S^{13}C^{15}N^{-}] + k_{SCN^{-} \to S^{13}C^{15}N^{-}}[SCN^{-}] - k_{S^{13}C^{15}N^{-} \to SCN^{-}}[S^{13}C^{15}N^{-}] \end{cases}$$
Eq.S1

In the equations, the time dependent populations were obtained from the vibrational energy exchange measurements. The lifetimes were determined by pump/probe experiments. The rate ratio  $k_{s^{13}c^{15}n^- \rightarrow scn^-} / k_{scn^- \rightarrow s^{13}c^{15}n^-} = e^{-75/205} = 0.69$  is determined by the detailed balanced principle. In analyzing the energy exchange rates with Eq.S1, we had only one unknown parameter,  $k_{scn^- \rightarrow s^{13}c^{15}n^-}$ .

## Calculation results with

$$\begin{aligned} k_{SCN^{-}fast} &= 1/3.0 \ (ps^{-1}); \ k_{SCN^{-}slow} = 1/22 \ (ps^{-1}); \\ k_{S^{13}C^{15}N^{-}fast} &= 1/3.6 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/31 \ (ps^{-1}); \\ k_{SCN^{-} \to S^{13}C^{15}N^{-}} &= 1/290 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-} \to SCN^{-}} = 1/418 \ (ps^{-1}); \\ A_{SCN^{-}fast} &= 0.19; \ A_{S^{13}C^{15}N^{-}fast} = 0.19 \end{aligned}$$

fit the four experimental curves very well, as shown in fig.4 C&D.

Kinetic parameters for fig.4E&F:

$$\begin{split} k_{SCN^{-}fast} &= 1/3.0 \ (ps^{-1}); \ k_{SCN^{-}slow} = 1/22 \ (ps^{-1}); \\ k_{S^{13}C^{15}N^{-}fast} &= 1/3.6 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/31 \ (ps^{-1}); \\ k_{SCN^{-} \to S^{13}C^{15}N^{-}} &= 1/290 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-} \to SCN^{-}} = 1/418 \ (ps^{-1}); \\ A_{SCN^{-}fast} &= 0.19; \ A_{S^{13}C^{15}N^{-}fast} = 0.19; \end{split}$$

To quantitatively analyze the energy transfer kinetics between the two CN stretches in DMF and D<sub>2</sub>O solutions (using KSCN/KS<sup>13</sup>C<sup>15</sup>N=1/1 in D<sub>2</sub>O as an example), we used a clusters based location-energy-exchange kinetic model that we developed before.<sup>5</sup> The

experiemental and fitting results for  $KS^{13}CN/KS^{13}C^{15}N=1/1$  in DMF solution with 1/8 salt molar ratio are shown in fig.S1. The details of the kinetic model and other data, including the nonresonant energy transfer in  $KSCN/KS^{13}CN=1/1$  and  $KSCN/KS^{13}C^{15}N=1/1$  DMF and D<sub>2</sub>O solutions, the resonant energy tranksfer of KSCN in DMF and D<sub>2</sub>O solutions can be found in our previous work.<sup>6</sup> Here, we also employed one conclusion we made before, that the ion cluster ratio in 1/8 DMF solutions is about 56%. Therefore, the equilibrium constant *K* is fixed at 1.27 during the fitting.<sup>6</sup>



**Figure S1.** The waiting time dependent intensities of (A) diagonal peaks and (B) cross peaks in the 2DIR spectra of  $KS^{13}CN/KS^{13}C^{15}N=1/1$  in DMF solution with 1/8 salt molar ratio. Dots are experimental data, and curves are calculations based on the energy exchange kinetic model.

The calculation parameters are

$$\begin{split} k_{S^{13}CN^{-}fast} &= 1/4.0 \ (ps^{-1}); \ k_{S^{13}CN^{-}slow} = 1/50.0 \ (ps^{-1}); \\ k_{S^{13}C^{15}N^{-}fast} &= 1/5.0 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/73.0 \ (ps^{-1}); \\ k_{clu \to iso} &= 1/10(ps^{-1}); \ k_{S^{13}CN^{-} \to S^{13}C^{15}N^{-}} = 1/225 \ (ps^{-1}); \\ A_{SCN^{-}fast} &= 0.12; \ A_{SCN^{-}slow} = 0.88; \\ A_{S^{13}C^{15}N^{-}fast} &= 0.01; \ A_{S^{13}C^{15}N^{-}slow} = 0.99; \\ K &= 1.27; \ D=0.88; \ offset = 0 \end{split}$$

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