Mode-specific intermolecular vibrational energy transfer. II. Deuterated water and potassium selenocyanate mixture

Hongtao Bian, Xiewen Wen, Jiebo Li, and Junrong Zheng^{a)} Department of Chemistry, Rice University, Houston, Texas 77005, USA

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Vibrational energy transfer from the first excited state (2635 cm⁻¹) of the O–D stretch of deuterated water (D₂O) to the 0-1 transition (2075 cm⁻¹) of the CN stretch of potassium selenocyanate (KSeCN) in their 2.5:1 liquid mixture was observed with a multiple-mode two dimensional infrared spectroscopic technique. Despite the big energy mismatch (560 cm⁻¹) between the two modes, the transfer is still very efficient with a time constant of 20 ps. The efficient energy transfer is probably because of the large excitation coupling between the two modes. The coupling is experimentally determined to be 176 cm⁻¹. An approximate analytical equation derived from the Landau–Teller formula is applied to calculate the energy transfer rate with all parameters experimentally determined. The calculation results are qualitatively consistent with the experimental data. © 2010 American Institute of Physics. [doi:10.1063/1.3458825]

I. INTRODUCTION

Vibrational energy transfer is a critical step of molecular reaction dynamics.^{1–5} In condensed phases, whenever a molecular bond is broken, formed, or changed into other conformations, a large part of the energy involved in the processes inevitably comes from or converts into vibrational energy. The vibrational energy flows from one mode to another inside a molecule, and from one molecule to another. Finally it dissipates away as heat. Vibrational dynamics in condensed phases have been extensively studied in both theory and experiments for decades.^{6–29} With advances of techniques, it is now possible that the time evolution of vibrational populations for almost every experimentally detectable vibration in a polyatomic solute can be monitored.^{6–8}

Most previous experiments were mainly focused on intramolecular relaxations. In intramolecular relaxations, the energy donors and acceptors (bright modes-experimentally detectable modes) inevitably overlap in frequency with many dark modes, e.g., combination bands with very low transition dipole moments. These dark modes can also serve as energy donors and acceptors, competing with the bright modes. The number of the dark modes is typically huge for a polyatomic molecule.^{25,30–33} Therefore, a seemingly intramolecular mode specific energy transfer from one mode to another is actually the sum from two bright modes and numerous dark modes. The experimentally determined energy transfer rate is the overall results of transfers among all the bright and dark modes, while the experimentally determined coupling constant is mainly between the bright modes. Such a situation makes it very difficult to properly experimentally investigate mode specific energy transfer processes. In addition, intramolecular relaxation induced combination bleaching and adsorption^{19,29,34,35} can make the analysis of intramolecular mode specific transfers even more complicated. Because of the difficulties, how the governing factors, e.g., coupling strength and energy mismatch, affect vibrational energy transfer kinetics, e.g., why a mode is a good energy acceptor and how fast it can accept energy directly from the donor mode, is relatively experimentally unexplored.

Well designed intermolecular mode specific vibrational energy transfers can in principle significantly relieve the competitions among the dark and bright energy donor/ acceptor pairs. A strategy is to use the donor and acceptor of a H-bond as the energy donor and acceptor, e.g., the stretch mode of OD as the energy donor and the stretch mode of CN as the acceptor for a OD···NC H-bond. Under this situation, it is still true that either OD or CN overlaps with many dark modes. However, the probability for the dark modes to efficiently compete as additional energy transfer channels from donors to acceptors is much smaller than the intramolecular cases. This is based on the assumption that the couplings between the dark modes overlapping with OD and the dark modes overlapping with CN are much weaker than the coupling between the stretches of OD and CN where the H-bond is. This assumption is reasonable, because the frequencies of the stretches of OD and CN change most among the bright modes when a H-bond forms. In intramolecular cases, there are no special reasons why the coupling between two bright modes must be stronger than the coupling between two dark modes or between one dark and one bright mode. There have been some findings about possible intermolecular mode-specific vibrational energy transfers.^{19,35,36} However, because of possible difficulties in experimental designs or techniques, why these mode-specific energy transfers are effective is largely unknown.

It is our intention to design a series of experiments to address how and why the vibrational energy of one mode on one molecule transfers to another mode on another molecule. The other purpose of our work on this topic is to accumulate knowledge about correlations between molecular structures and vibrational energy transfer kinetics and pathways. The

^{a)}Author to whom correspondence should be addressed. Electronic mail: junrong@rice.edu.

knowledge will be indispensable for nonlinear IR techniques, e.g., two dimensional (2D) IR, to determine static or transient molecular structures on three dimensions, if one day these techniques are mature enough to do the job. In our previous work,³⁷ we found that the energy transfer between two modes with an energy mismatch of 97 cm⁻¹ is very slow $(\sim 330 \text{ ps})$ despite the relatively big excitation coupling between the two modes ($\sim 18 \text{ cm}^{-1}$). Quasiresonant energy transfers with smaller couplings are ten times faster.^{19,35} The huge rate difference implies the significant effect of energy mismatch on the transfer rate. To further investigate how the coupling strength and energy mismatch interplay, in this work, we designed a system which has one of the strongest intermolecular interactions-ion/water interaction but with a very big energy mismatch (560 cm^{-1}) between the energy donor and acceptor. In the system-a saturated KSeCN D₂O solution with a molecular ratio $D_2O/KSeCN \sim 2.5/1$ (the CN stretch of KSeCN has a very long vibrational lifetime, which is probably because of the arguable heavy atom effect^{31,37,38}), the OD stretch 0-1 transition (2635 cm^{-1}) is the energy donor and the CN stretch 0-1 transition (2075 cm^{-1}) of SeCN⁻ is the acceptor. In addition, the system is also a very good example to demonstrate how intermolecular vibrational couplings, energy transfers and relaxations, heat, or photoproducts affect the appearances of pure absorptive 2D IR spectra.

II. EXPERIMENTS

The optical setup is described previously.³⁷ Briefly, a picosecond amplifier and a femtosecond amplifier are synchronized with the same seed pulse. The synchronization jitter is smaller than 150 fs, as measured from the cross correlation of the two amplifiers' outputs. The picosecond amplifier pumps an optical parametric amplifier (OPA) to produce ~ 1 ps mid-IR pulses with a bandwidth of ~ 21 cm⁻¹ (tunable) in a tunable frequency range from 900 to 4000 cm^{-1} with energy of $10-40 \ \mu J/pulse$ at 1 KHz. The femtosecond amplifier pumps another OPA to produce ~ 140 fs mid-IR pulses with a bandwidth of $\sim 200 \text{ cm}^{-1}$ in a tunable frequency range from 900 to 4000 cm⁻¹ with energy of 10-40 µJ/pulse at 1 KHz. In 2D IR and pump/probe experiments, the picosecond IR pulse is the pump beam (pump power is adjusted based on need). The femtosecond IR pulse is the probe beam which is frequency resolved by a spectrograph yielding the probe axis of a 2D IR spectrum. Scanning the pump frequency yields the other axis of the spectrum. Two polarizers are added into the probe beam path to selectively measure the parallel or perpendicular polarized signal relative to the pump beam.^{39,40} Vibrational lifetimes are obtained from the rotation-free 1-2 transition signal $P_{\text{life}} = P_{\parallel} + 2 \times P_{\perp}$, where P_{\parallel}, P_{\perp} are parallel and perpendicular data, respectively. Rotational relaxation times are acquired from $\tau = P_{\parallel} - P_{\perp} / P_{\parallel} + 2 \times P_{\perp}$. Viscosities were measured with a Cannon-Fenske kinematic viscosity tubes, American Society for Testing and Materials (ASTM) size 25, at 23 °C under which the ultrafast experiments were conducted.

All chemicals were purchased from Aldrich and used as



FIG. 1. (a) FTIR spectra of D_2O and a $D_2O/KSeCN$ mixture and [(b) and (c)] 2D IR spectra of the $D_2O/KSeCN$ mixture at waiting time 0. The spectra show that the stretch frequency of OD associated with SeCN⁻ is 2635 cm⁻¹.

received. Temperature dependent Fourier transform infrared spectroscopy (FTIR) measurements were performed with a ThermoFisher FTIR spectrometer and a temperature controller from Harrick Scientific.

The structures were determined with density functional theory (DFT) calculations.⁴¹ The DFT calculations were carried out as implemented in the GAUSSIAN 98 program suite. The level and basis set used were Becke's three-parameter hybrid functional combined with the Lee–Yang–Parr correction functional, abbreviated as B3LYP, and 6-31+G(d,p). All results reported here do not include the surrounding solvent and therefore are for the isolated molecules.

III. RESULTS AND DISCUSSION

A. Static information of the $D_2O/SeCN^-$ complex in solution

1. Vibrational frequency of OD associated with SeCN⁻ ion

Figure 1 displays the FTIR and 2D IR spectra of the D₂O/KSeCN mixture and a pure D₂O liquid sample. The CN stretch frequency is 2075 cm⁻¹. The OD stretch is a broad band in pure water. The addition of KSeCN salt blueshifts and narrows the broad band and splits it into two peaks [Fig. 1(a)]. From the FTIR spectrum, it is difficult to distinguish which OD peak is associated with the SeCN⁻ ion. 2D IR spectra in Figs. 1(b) and 1(c) clearly show that the OD peak at 2635 cm⁻¹ with a width of ~ 15 cm⁻¹ is strongly associated (coupled) to the CN stretch of the SeCN- ion. In Fig. 1(b), the two peaks are purely from the DOD/SeCN⁻ complex. The x-coordinate (2075 cm⁻¹) of the peaks represents the CN stretch and the y-coordinate (2635 cm^{-1}) of the red peak represents the OD stretch strongly coupled to the SeCN- ion. The origin of the peaks can be qualitatively understood in the following way. When a SeCN⁻ ion is excited to vibrate at its frequency of 2075 cm⁻¹, the water molecule



FIG. 2. Two calculated complexes between a water molecule and a SeCN⁻ ion in gas phase. (a) is more stable than (b) by ~ 2.3 kcal/mol. The calculated angle θ between the OD bond and the CN bond in (a) is 10°. The calculated angles θ_1 and θ_2 between the OD bond and the CN bond in (b) are 36° and 42°, respectively.

associated with it immediately feels the CN vibration and changes its vibrational frequency from 2635 to 2605 cm⁻¹ and produces a new absorption at this new frequency (the blue peak). At the same time, the water frequency shift leaves a ground state hole which allows more IR radiation at the old frequency of 2635 cm⁻¹ to go through the sample (the red peak). More rigorously speaking, the red peak comes from the combination band (OD+CN) ground state bleaching, and the blue peak is from the combination band absorption.^{42,43} The Feynman diagrams showing the origins of the peaks are in the supporting materials. A similar explanation is applied to Fig. 1(c). The difference is that in Fig. 1(c), the excitation (pump) is OD and the sensor (probe) of the excitation is CN.

2. Possible structure of D₂O/SeCN⁻ complex

DFT calculations show that one water molecule can form two possible complexed structures [Figs. 2(a) and 2(b)] with a SeCN⁻ ion in gas phase. The complex in Fig. 2(a) (formation energy of -14.6 kcal/mol) is more stable than the one in Fig. 2(b) (formation energy of -12.3 kcal/mol). The calculated angle θ between the OD bond and the CN bond in Fig. 2(a) is 10°. The calculated angles θ_1 and θ_2 between the OD bond and the CN bond in Fig. 2(b) are 36° and 42°, respectively. In principle, the angles can be determined by measuring the anisotropies of the peaks in Fig. 1(b) or Fig. 1(c).^{44,45} However, what is obtained from the anisotropy measurements is the angle between the transition dipole vectors of the two vibrational modes. These vectors may or may not overlap with the bonds' directions. According to DFT calculations, in SeCN⁻ ion, the CN stretch transition dipole vector is almost along with the CN bond direction. In D₂O, the OD stretch transition dipole vectors are not along with the OD bond directions, but in HOD, they do almost overlap. Therefore, a saturated KSeCN solution (molecular ratio D₂O/KSeCN~2.5/1) in a water mixture with a very small D₂O/H₂O ratio is straightforward to determine the relative bond angles.

To determine the relative orientation of the OD bond and the CN bond of the water/SeCN⁻ complex, we measured the waiting time dependent anisotropies [Fig. 3(c)] of the combination band blue peak (2075 cm⁻¹, 2607 cm⁻¹) in Fig. 3(b) of a saturated KSeCN solution in D₂O/H₂O (1 wt %) mixture. Data from the red peak (2075 cm⁻¹, 2636 cm⁻¹) are not used in the analysis, because we found that it contains some nonresonant signal which alters the anisotropy measured at short waiting times. In two coupled modes, the anisotropy *R* of their combination band peak is correlated with the angle θ between their transition dipole moments in the form of⁴⁴

$$R = \frac{3\cos^2\theta - 1}{5}.$$

At times 0–0.2 ps, $R=0.37\pm0.02$ from the measurements in Fig. 3(c). From Eq. (1), the angle between the transition dipole moments of OD of HOD and CN of SeCN- of the HOD/SeCN⁻ complex is determined to be $12^{\circ} \pm 5^{\circ}$. According to DFT calculations, the angle between the OD and CN bonds is almost identical to the angle between their transition dipole moments, which is 10° in the complex shown in Fig. 2(a). The calculated angles in the complex in Fig. 2(b) are 36° and 42°, respectively. The experimental result favors the more stable complex structure in Fig. 2(a). However, we believe that the consistency between experimental and calculated data here would be more appropriate to be considered as coincidence, since the calculations were performed for gas phase molecules, while experiments are for liquid molecules. In the liquid, it is probably true that more than one water molecules are bound to the SeCN- ion with different binding strength. What the 2D IR measures is the overall binding result of the water molecules weighing by their coupling strength to the CN stretch, rather than a single water/ion H-bond unless the signal from this bond is dominant. A high level calculation in the liquid phase would be necessary to



FIG. 3. (a) FTIR spectrum of a saturated KSeCN solution in D_2O/H_2O (1 wt %) mixture; (b) 2D IR spectra of the solution showing the CN/OD cross peaks at waiting times of 0.5 and 1 ps; (c) waiting time dependent anisotropies of the blue peak (2075 cm⁻¹, 2607 cm⁻¹) in (b).



FIG. 4. (a) Waiting time dependent 2D IR spectra of OD and CN stretches of the $D_2O/SeCN^-$ complex; (b) energy level diagram of the OD/CN system [transitions by straight arrows only count for the last two interactions (probe frequency) in experiments]. In the 2D IR spectra, the intensities of CN 0-1 and 1-2 peaks 1 and 2 are divided by 14.4. In (b), the wavy curves show the origin of the OD \rightarrow CN energy transfer peak 9 (in Fig. 13). This peak almost overlaps with peak 8 since both peaks have the same x-coordinate and their y-coordinates are only 3 cm⁻¹ different; (c) graphical representation of the OD to CN vibrational energy transfer and 2D IR data.

further explore the water structures on the ion surface. Nonetheless, the comparison between this simple DFT calculation and experimental data provides us a qualitative picture about a possible major H-bond structure of the SeCN⁻/D₂O complex.

From Fig. 3(c), the randomization time constant of the transition dipole cross angle of the HOD/SeCN⁻ complex is 4.0 ± 1 ps. This constant is very close to, but a little faster than, the rotational time constants of the two components of the complex. The rotational time constant of HOD is determined to be 5.8 ± 1 ps. The rotational time constant of SeCN⁻ is determined to be 4.5 ± 0.6 ps (data, see Fig. 5).

3. Coupling strength between OD and CN

The vibrational energy transfer from the OD stretch 0-1 transition to the CN 0-1 transition is largely determined by the coupling between the initial state and the final state $\beta_{\rm OD-CN} = \langle 1_{\rm OD} 0_{\rm CN} | V | 0_{\rm OD} 1_{\rm CN} \rangle = \langle 1_{\rm OD} | V | 1_{\rm CN} \rangle$. This coupling can be experimentally determined assuming transition dipole coupling mechanism, based on 2D IR measurements and an excitation exchange model.⁴⁶ According to the model,^{26,46,47} the coupling is correlated with the anharmonicities of the OD stretch $\Delta_{\rm OD} = \omega_{\rm OD1-2} - \omega_{\rm OD0-1} = 85$ cm⁻¹, the CN stretch $\Delta_{\rm CN} = \omega_{\rm CN1-2} - \omega_{\rm CN0-1} = 33$ cm⁻¹, and the OD/CN combination



FIG. 5. Anisotropy decays of ion-bound OD in a $D_2O/KSeCN 2.5/1$ mixture (a), in a $H_2O/KSeCN 2.5/1$ mixture with 1% D_2O (b), and CN in a $D_2O/KSeCN 2.5/1$ mixture (c), and in a 0.2% KSeCN D_2O solution (d).

band shift $\Delta_{\text{OD/CN}} = \omega_{\text{CN0-1}} - \omega_{1_{\text{OD}} - \text{OD/CN}} = 30 \text{ cm}^{-1}$, and their 0-1 transition frequencies $\omega_{\text{OD0-1}} = 2635 \text{ cm}^{-1}$, and $\omega_{\text{CN0-1}} = 2075 \text{ cm}^{-1}$ with the following equation:

$$\Delta_{\rm OD/CN} = \frac{2\beta_{\rm OD-CN}^2 (\Delta_{\rm OD} + \Delta_{\rm CN})}{(\omega_{\rm OD0-1} - \omega_{\rm CN0-1})(\omega_{\rm OD0-1} - \omega_{\rm CN0-1})}.$$
 (2)

The derivation of Eq. (2) is provided in the supporting materials. All parameters in Eq. (2) for the $D_2O/SeCN^$ complex are experimentally determined, see Fig. 4. The equation yields $\beta_{OD-CN}=200$ cm⁻¹. A more precise treatment to obtain the coupling constant in the local mode basis can be obtained by directly diagonalizing the Hamiltonian matrix of the system (see supporting materials). The OD/CN combination band shift $\Delta_{\rm OD/CN} = \omega_{\rm CN0-1} - \omega_{\rm 1_{OD}} - OD/CN}$ =30 cm⁻¹ is determined by the position difference between the red peaks and blue peaks along the probe axis at an early waiting time before the spectral diffusion occurs in Figs. 1(b) and 1(c). The full width at half maximum of CN is 36 cm^{-1} from FTIR measurement in Fig. 1(a). The peak width along the pump axis is a little bigger than this value in Fig. 1(b) because of the bandwidth of the pump pulse. The CN band is inhomogeneously broadened, as we can see from the elongated line shapes of peaks in Figs. 1(b) and 3(b) and spectra at early waiting times in Fig. 6. The homogeneous linewidth of CN is only \sim 15 cm⁻¹ from the early waiting time (e.g., 0 ps) 2D IR spectra in Fig. 6.

B. Dynamic information

In the $D_2O/SeCN^-$ mixture, several fast dynamics are coupled and affect the 2D IR signal: the spectral diffusion, the exchange between ion-bound and unbound water molecules, the vibrational energy exchange between the asymmetric and symmetric stretches of D_2O , heating from the vibrational relaxation, rotational relaxation of molecules, and the energy exchange between the OD stretch and the CN stretch of the two molecules. To quantitatively analyze the mode specific vibrational energy transfer dynamics between OD and CN, the effects and kinetics of other dynamic processes listed above must be known beforehand.



FIG. 6. Time dependent 2D IR spectra of a $D_2O/KSeCN 2.5/1$ mixture showing the CN stretch 0-1 and 1-2 transitions. The peaks correspond to peaks 1 and 2 in Fig. 4(a). The frequency shifts of the peaks with time are caused by heat from the CN vibrational relaxation.

1. Rotational dynamics and self vibrational exchanges

The rotational dynamics of the ion-bound OD can not be obtained directly from the anisotropy measurements in the D₂O/KSeCN mixture, because the resonant or quasiresonant vibrational energy transfers among ODs can facilitate anisotropy decay.⁴⁸ Separating OD from each other with H₂O can remove the effect of energy transfers and recover the rotational dynamics. Figure 5 displays the anisotropy decays of ion-bound OD in a D₂O/KSeCN 2.5/1 mixture (a), in a $H_2O/KSeCN$ 2.5/1 mixture with 1% D_2O (b), and CN in a D₂O/KSeCN 2.5/1 mixture (c), and in a 0.2% KSeCN D₂O solution (d). From Fig. 5(a), the OD anisotropy decays with a time constant of 1.7 ± 0.1 ps in the pure D₂O salt solution, while in a dilute OD solution [Fig. 5(b)], it is 5.8 ± 1 ps. The 5.8 ps is the rotational time constant of the ion-bound OD, which is consistent with a recent measurement on another salt solution.⁴⁹ The results also indicate that the vibrational energy exchange among the ODs in the pure D₂O salt solution is <1.7 ps. The energy exchange can be seen clearly from the growth of red cross peaks in Fig. 7. Situations are different on the CN side. In the D₂O/KSeCN 2.5/1 mixture (c), the anisotropy decay of CN is 4.5 ± 0.6 ps. In a 0.2% KSeCN D₂O solution, it decays faster, with a time constant of 4.0 ± 0.3 ps. The viscosity of the D₂O/KSeCN 2.5/1 mixture is about 30% higher than that of the 0.2% KSeCN/ D_2O solution. The viscosity difference counts for the difference between the anisotropy decays. The decay constants also imply that the resonance energy transfer among SeCN⁻ ions is not fast. It should be slower than 4.5 ± 0.6 ps (if any), in the D₂O/KSeCN 2.5/1 mixture. This result is not very surprising since the ions are surrounded and separated by water molecules. All the inertial anisotropy values in Fig. 5 are smaller than 0.4. There are two possible reasons. The first one is a possible ultrafast inertial rotational decay component (within 200 fs), whose amplitude is dependent on the angular potential of the molecule.^{50,51} The ultrafast inertial rotational decay component is frequency dependent. The slow rotational decay time constant (>1 ps) is independent of the inertial

decay amplitude.^{50,51} The second is the nature of the narrowpump/broad-probe scheme of our experiments, a significant portion of the inertial signal from time zero is from delays of 200–300 fs. The two possible reasons (especially the ultrafast inertial decay) can make the structure determined by Eq. (1) have a very big uncertainty range. Another possible reason for the small inertial anisotropy values, overpumping, is ruled out by the power dependent measurements. Data are in the supporting materials.

The molecular rotations make the 2D IR signal smaller, which can add complexity in analyzing the OD/CN vibrational energy transfer.³⁵ Experimentally, we can manage to obtain rotation free data $(P_{\text{life}} = P_{\parallel} + 2 \times P_{\perp})$ so that rotation is not an issue in our energy transfer kinetics analysis anymore. The resonance energy transfer (if any) among SeCN⁻ ions does not affect the 2D IR signal, since the transfer is short range (nanometer) while the signal spot size is much bigger (~200 μ m). It can be omitted in the OD/CN vibrational exchange analysis. The energy transfers among ODs do affect the 2D IR signal. It will reduce the population of the ion-bound OD excitation, because all OD stretches span $\sim 200 \text{ cm}^{-1}$ broad while the bandwidth of the excited ionbonded OD is only ~ 15 cm⁻¹. The effect can be simply treated as an apparent vibrational decay of OD in analyzing the OD/CN energy transfer kinetics, because 1.7 ps is much faster than the transfer from OD to CN (20 ps, in the kinetics analysis part).

2. Spectral diffusion and OD chemical exchange

The spectral diffusion characterizes frequency fluctuations caused by molecular motions of the solvent. Because of the spectral diffusion, the line shape of a diagonal peak in a 2D IR spectrum evolves from elongated along the diagonal to round (or the slope is from 45° to 0°) with time.^{52–54} Such a peak shape evolution can be utilized to obtain the spectral diffusion time.^{52,54} Figures 6 and 7 display the time evolutions of the CN and OD diagonal peaks of the D₂O/KSeCN 2.5/1 mixture. Figure 8 displays time evolutions of the OD diagonal peaks of the H₂O/KSeCN 2.5/1 mixture with 1%



FIG. 7. Time dependent 2D IR spectra of a $D_2O/KSeCN 2.5/1$ mixture showing the OD stretch transitions. The growth of the cross peaks is from vibrational energy exchange and heat from the vibrational relaxation.

D₂O. At very short times, e.g., 0 ps, all red diagonal peaks elongate along the diagonal (the slope is ~45°). The peak shapes then evolve to be round or square (the slope is ~0°). At a glance, it takes about 5 ps for the peak shape changes (spectral diffusion) to be complete. The results indicate that within 5 ps, the solvent molecules have sampled most possible configurations. To quantitatively analyze the spectral diffusion time, we follow the dynamic linewidth approach.⁵² The time dependent dynamic linewidth [in Fig. 8(b)] from Fig. 8(a) shows that at 1.9 ps (turning point), the linewidth has already reached 95% of the long-time asymptotic linewidth of 146 cm⁻¹.

In addition to spectral diffusion, some other time dependent features also appear in 2D IR spectra of the $D_2O/KSeCN 2.5/1$ mixture, e.g., growth of cross peaks and peak frequency shifts. These features are caused by heats and vibrational energy and chemical exchange from the vibrational relaxations, elaborated in the following paragraphs.

In the D₂O/KSeCN 2.5/1 mixture, not all the D₂Os are bound to SeCN⁻ ions. The bound and unbound D₂O are under constant exchange. Recent echo 2D IR experiments on salt waters show that this type of water molecule exchange occurs within a few picoseconds.^{49,55} Similar dynamics was also observed in the water/KSeCN 2.5/1 mixture. In Fig. 8, the growth of cross peaks (b) and (c) is from the chemical exchange between the SeCN--bound and unbound water molecules. A simple investigation on the growth of the cross peaks in Fig. 8 clearly shows that the exchange occurs within a few picoseconds. An interesting observation about the system is that the ion-bound peak in FTIR is prominent [Fig. 3(a), but it is almost invisible in the 2D IR spectra [peak (A) in Fig. 8]. This is caused by the small OD transition dipole moment ratio of ion-bound ODs over those unbound ones of the system, which is different from the other two OD/ion complexes.^{49,55} [One previous experiment repeated with our technique and actually got almost identical results as published (see supporting materials).⁴⁹]

In our "hole-burning type" 2D IR experiments, the spectral width of either CN or OD is wider than the bandwidth of the pump beam. The spectral diffusion therefore reduces the population at the pump frequency. For a similar reason, the chemical exchange between the ion-bound and unbound OD can also reduce the ion-bound OD vibrational excitation population. These processes all occur within a few picoseconds. Therefore, we can consider them simply as some decaying factors of the apparent vibrational decay of the OD excitation in the kinetic analysis for the vibrational energy transfer between CN and OD.

3. Effects of vibrational relaxations and heat on 2D IR spectra

The vibrational relaxation of a high-frequency mode typically has two effects on a bulk sample: exciting low-frequency modes and heating up the sample. The excitations of low-frequency modes can induce relaxation combinational band bleachings and absorptions.^{19,34,35,56} Heating from vibrational relaxations produces three results: heat induced transparency, absorption frequency shifts, and photoproducts, e.g., H-bond breaking.^{35,37,57} In 2D IR spectra, all these effects from vibrational relaxations produce various bleaching (red) and absorption (blue) peaks and peak frequency shifts. These changes in the 2D IR spectra of the D₂O/KSeCN 2.5/1 mixture will be manifested in the following paragraphs.

First, let us look at the OD diagonal block in Fig. 9 (Fig. 7). At very short times, e.g., 0 ps, the OD stretch 0-1 transition is a broad peak along the diagonal. Up to 2 ps, offdiagonal peaks grow in, resulting from the spectral diffusion, OD vibrational exchange, chemical exchange, and heat effect from OD relaxations. Up to 4 ps, a photoproduct absorption peak at probe frequency of 2685 cm⁻¹ and two photoproduct bleaching peaks at probe frequencies of 2600 and 2500 cm⁻¹ appear. This feature then lasts for more than 1 ns. The photoproduct peaks come from the H-bond breaking induced by the OD vibrational relaxation heat, following the explanation for OD in H₂O:⁵⁷ after the OD is excited, its vibrational energy relaxes within 1–2 ps (data, see the kinetics analysis part).^{58,59} The vibrational energy finally converts into heat



FIG. 8. (a) Time dependent 2D IR spectra of a $H_2O/KSeCN 2.5/1$ mixture with 1% D_2O showing the OD stretch transitions. The growth of the cross peaks (b) and (c) is from the chemical exchange between the ion-bound and unbound OD. The diagonal peak (a) is from the ion-bound OD, which has a prominent FTIR peak in Fig. 3(a). The different amplitude ratios of (a) over the bound OD in FTIR and 2D IR are caused by the small transition dipole moment of the ion-bound OD. (b) Waiting time dependent dynamic linewidth from (a).

within a few picoseconds. Because of the heat, some strong H-bonds break and form some weakly bonded or even free bonded OD species. The H-bond breaking produces bleachings at the H-bonded OD symmetric stretch of ~2600 cm⁻¹ (peak 11) and asymmetric stretch of ~2500 cm⁻¹ (peak 12). The nascent ODs appear at a higher frequency of 2685 cm⁻¹ for the asymmetric stretch and a possible frequency of ~2570 cm⁻¹ for the symmetric stretch. The ODs are new species and therefore will absorb lights at these two frequencies and form blue absorption peaks at 2685 cm⁻¹ (peak 10) and ~2570 cm⁻¹ (peak 13) which overlap with the two bleaching red peaks. The photoproduct absorption peak 10 grows with a time constant of 2.8 ps after pumping the ion-

bound OD at 2635 cm⁻¹, see Fig. 10 (full pump-probe spectrum in supporting information). It is interesting to note that the photoproduct absorption peak in pure D_2O also appears at 2685 cm⁻¹ (data in SI).

Similar photoproduct peaks are also observed on the CN-pump/OD-probe cross block (peaks 5, 6, 14, 15, and 16). At short times, e.g., 0 ps, the appearances of peaks 5 and 6 are due to the coupling between the CN and OD as described above. These two peaks then diminish with the vibrational decay time constant of CN, since they are purely from the excitation of CN, and the SeCN⁻ ions are always bound to OD. At longer times, e.g., 20 or 30 ps, the photoproduct peaks 14, 15, and 16 grow in. These peaks are induced by



FIG. 9. Waiting time dependent 2D IR spectra of OD and CN stretches of the $D_2O/SeCN^-$ complex. In the 2D IR spectra, the intensities of CN 0-1 and 1-2 peaks 1 and 2 are divided by 14.4.

heat from the CN vibrational relaxation. Since the vibrational excitation of CN in the mixture decays much slower than that of the OD stretch, the growths of the photoproduct peaks 14-16 are therefore slower than those of peaks 10-13. Figure 11 displays the decays of peak 2 and the growth of peak 14. The decay of peak 2 [CN vibrational relaxation, Fig. 11(a) is a biexponential with a fast time of 4 ps (22%) and a slow time of 100 ps (78%). This behavior is considerably different from what is observed for the CN vibrational relaxation in a dilute D_2O solution. In the dilute solution, it is a single exponential with a time constant of 37 ps (data in SI), consistent with a reported value of 38 ps.⁶⁰ Figure 11(b)displays the growth of the photoproduct peak 14 and the rescaled decay of peak 2 with a flipped sign. Although peak 14 originates from the decay of peak 2, the growth and the decay of these two peaks are not identical. Only after the vibrational relaxation of CN is equilibrated into heat after 300 ps, the two processes have the same dynamics, which is similar to what we have observed for another system.³⁷ The appearances of these photoproduct peaks have a side effect on our experiments. Because of the severe frequency overlapping with these photoproduct peaks, the effect of the possible direct vibrational energy transfer from CN to OD (if any) can not be experimentally determined.

In the CN diagonal block (peaks 1 and 2 in Figs. 6 and 9), at long waiting times, e.g., 500 ps, the red peak in Fig. 6 shifts to a higher frequency of $\sim 2082 \text{ cm}^{-1}$, and the 1-2 blue peak disappears. A new weak broad blue peak appears at $\sim 2050 \text{ cm}^{-1}$. The disappearance of the 1-2 transition peak demonstrates that the vibrational excitation of CN has relaxed, which is consistent with the vibrational lifetime measurement. The red peak at $\sim 2082 \text{ cm}^{-1}$ is the induced transparency by heat from the CN vibrational relaxation, and the weak blue peak is from the heat induced absorption.

The heat effects from the vibrational relaxations on the CN and OD regions of the 2D IR spectra described above can be confirmed with temperature difference FTIR measurements. Figure 12 displays the temperature difference FTIR spectra of the $D_2O/KSeCN 2.5/1$ mixture in the CN and OD frequency ranges. The spectra were obtained by subtracting



FIG. 10. Rotation-free pump (2635 cm⁻¹)/probe (2685 cm⁻¹) data showing the photoproduct peak at $\omega_{\text{probe}} = 2685$ cm⁻¹ in Figs. 7 and 8 grow with a time constant of 2.8 ps.



FIG. 11. (a) The vibrational decay of peak 2 in Fig. 9; (b) the growth of the photoproduct peak 14 and the rescaled decay of peak 2 with a flipped sign.

the room temperature (24 °C) spectrum from higher temperature spectra. In Fig. 12(a), increasing temperature produces a strong bleaching at ~2082 cm⁻¹ and a weak absorption at ~2050 cm⁻¹. In Fig. 12(b), increasing temperature produces two bleachings at ~2600 and 2500 cm⁻¹ and one absorption at ~2685 cm⁻¹. These observations are consistent with what is demonstrated from 2D IR spectra. According to our experimental conditions, the temperature increase in the 2D IR measurement is estimated to be ~10 °C.

Heat effects on peaks 7–9 are similar to what are on the CN peaks 1 and 2. The appearances of heat induced transparency and absorption appear earlier at peaks 7–9 (Fig. 13) than peaks 1 and 2 (Fig. 6), since heats on peaks 7–9 are from the OD vibrational relaxations, which are much faster than the CN decay. In addition to the heat effect, the direct vibrational energy transfer from OD to CN also produces cross peaks in the positions of peaks 7–9. It will be elaborated in next paragraphs.

4. Energy transfer from OD to CN

Three possible mechanisms can generate cross peaks (Fig. 13) in the positions of peaks 7 and 8, resulting from the OD-pump/CN-probe. The first one is the coupling between the OD and CN modes. The coupling produces the ground state bleaching peak 7 and the combination band absorption peak 8 even at time 0. Feynman diagrams (in SI) show that these two peaks must decay with the apparent ion-bound OD vibrational lifetime of 1.5 ps (data in the kinetics analysis

part). The apparent vibrational lifetime is the result of vibrational decay, energy transfers, spectral diffusions, and chemical exchanges. If this was the only origin of peaks on the position, we should not see any peaks after 5 ps. In Fig. 13, peaks are still clearly visible, demonstrating that there must be some other origins for the peaks. The second possible origin of the cross peaks is heating from the vibrational relaxation of OD. The heat induced peaks must grow at the same rate of heat generation whose time constant is 2.8 ps (from Fig. 10). The appearances of these heat induced peaks must be similar to those in Fig. 6 at long times, e.g., 1000 ps. In other words, if coupling and heating are the only origins for the cross peaks in Fig. 13, we should see peaks after 5 ps in Fig. 13 similar to the one at 1000 ps in Fig. 6. The existence of peak at (2635 cm⁻¹, 2042 cm⁻¹) up to 200 ps in Fig. 13 demonstrates that there must be a third origin for the peaks. The origin is the mode specific vibrational energy transfer from OD to CN. Feynman diagrams (in SI) show that peaks from this energy transfer origin grow at the energy transfer rate and decay with the CN vibrational lifetime. This the reason that even at 200 ps, peak at is $(2635 \text{ cm}^{-1}, 2042 \text{ cm}^{-1})$ is still visible in Fig. 13.

From the above analysis, peaks on the positions of peaks 7 and 8 have three origins. These peaks are severely overlapped: peak 7 (2635 cm⁻¹, 2075 cm⁻¹) and peak 8 (2635 cm⁻¹, 2045 cm⁻¹) are from coupling; peak 17 (2635 cm⁻¹, 2082 cm⁻¹) and peak 18 (2635 cm⁻¹, 2050 cm⁻¹) are from heating; peak 7 (2635 cm⁻¹, 2075



FIG. 12. Temperature difference FTIR spectra of the $D_2O/KSeCN$ 2.5/1 mixture in the CN (a) and OD (b) frequency ranges. Positive values represent absorption and negative values represent bleaching.



FIG. 13. Time dependent 2D IR spectra with OD-pump and CN-probe. Each plot is normalized to its own maximum intensity. Each contour is a 10% amplitude change. The time dependent intensity change at the pump frequency of 2635 cm⁻¹ is provided in supporting materials Fig. S8.

 cm^{-1}) and peak 9 (2635 cm^{-1} , 2042 cm^{-1}) are from energy transfer. It seems very complicated to extract energy transfer kinetics from either peak 7 or 9 (peak 9 is much better since most of the peak intensity between 5-100 ps is from energy transfer) because of the spectral overlapping. In fact, it turns out to be very straightforward, because the coupling and heating peaks have experimentally well defined amplitudes and decay and rising time constants. For the coupling peak 8, its maximum amplitude is the amplitude of the blue peak 8 at time 0 in Fig. 13, it then decays exponentially with the OD apparent vibrational lifetime of 1.5 ps. For the heating peak 18, it starts from 0, and then grows exponentially with the heat generation time constant of 2.8 ps to its maximum intensity which is measured at 1000 ps in Fig. 13 (\sim 7% of the heat generated much slower from CN which obtains energy from OD). From the parameters, the time dependent intensities of coupling and heating peaks at the probe frequency of 2042 cm^{-1} can be constructed. The time dependent intensity of peak 9 purely from the mode specific energy transfer can therefore be obtained by subtracting these constructed intensities from the measured apparent intensity at the probe frequency of 2042 cm⁻¹. Results are displayed in Fig. 14. The energy transfer peak grows to a maximum at 6.5 ps and then decays with a time constant of ~ 100 ps [Figs. 14(b) and 14(d)]. The maximum appearance time of 6.5 ps is not the energy transfer time constant $t=1/k_{OD\rightarrow CN}$ which will be obtained in the kinetics analysis part.

C. Kinetics analysis

To quantitatively analyze the energy transfer kinetics between OD and CN, we construct a kinetic model³⁷ based on the biexponential decay of the CN stretch. In the model, OD and CN can exchange vibrational energy, and they also decay with their own apparent vibrational lifetimes. Experimental data are rotation free. Therefore, the model does not contain any rotational component. The model can be illustrated in the following scheme:

$$\overset{k_a}{\leftarrow} OD \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} CN \overset{k_b}{\rightarrow}$$

where k_a and k_b are the vibrational lifetimes of OD and CN, respectively, and k_{ab} and k_{ba} are the energy exchange rate constants. Because the CN decay is biexponential, we separate the SeCN⁻ into two subgroups. The weighing of each subgroup is determined by the prefactors of the biexponential. Each subgroup has a single-exponential-decay lifetime. Each can exchange energy with OD, but the subgroups can not exchange energy with each other (this follows the assumed physical picture of biexponential: the subcomponents can be considered as independent species). In the model, the effects of dynamics, chemical exchanges, spectral diffusions, vibrational decays, and vibrational exchanges within each species, are simply treated as apparent vibrational decays as experimentally measured. This treatment is based on two facts: (1) all the dynamics are much faster than the OD/CN energy transfer and (2) the energy up-pumping from CN to OD is so small that it is negligible, resulting in that all other dynamics of OD only affect the growth rate of the energy transfer peak 9, but not its decaying rate.

In calculating the OD/CN energy transfer rates based on the model, the time dependent OD and CN populations are provided by the normalized intensities of the ion-bound OD 0-1 peak 3, and OD to CN cross peak 9. The normalization of the OD to CN cross peak population is obtained by dividing the intensity of peak 9 by the transition dipole ratio square, $\mu_{CN12}^2/\mu_{OD01}^2$ =6.6. The ratio is obtained from the FTIR measurements [peak ratio in Eq. (3)] and the 2D IR measurements [ratio of peak 2/peak 3 at time 0, Eq. (4)],



FIG. 14. Time dependent intensity of peak 8 at probe frequency of 2042 cm⁻¹. (a) Peak intensity and its three components: coupling intensity, heating intensity, and energy transfer intensity; (b) time dependent intensity purely from the OD to CN energy transfer. Experimental and calculation results of the OD to CN vibrational energy transfer kinetics analysis from peaks 3 (c) and 9 (d) in Fig. 9.

$$\frac{C_{\rm CN}\mu_{\rm CN01}^2}{C_{\rm OD}\mu_{\rm OD01}^2} = 1.1$$
(3)

and

$$\frac{C_{\rm CN}\mu_{\rm CN01}^2\mu_{\rm CN12}^2}{C_{\rm OD}\mu_{\rm OD01}^4} = 7.3,$$
(4)

where C_i is the concentration and μ is the 0-1 or 1-2 transition dipole moment. The possible CN to OD transfer peak is totally overwhelmed by the heating effects (peaks 14–16). Therefore, this peak and the CN 1-2 transition peak 2 were not used to extract the energy up-pumping rate constant k_{ba} .

None of the four parameters, k_a , k_b , k_{ab} , and k_{ba} , is known beforehand. The vibrational lifetimes of the OD and CN can not be predetermined in their pure liquids, because different solvents can change the lifetimes substantially. If these four parameters are allowed to vary freely in calculations, then calculation results would be somehow arbitrary. Luckily, many constraints can be applied to limit the ranges of the parameters based on experimental results. First of all, the vibrational lifetimes of OD and CN in the mixture must be very close to their apparent lifetimes (the rotation-free decay time constants of peaks 2 and 3), because the vibrational energy involved in the mode specific vibrational exchange is only ~7% of the initial excitation energy. Therefore, in calculating the data, we allowed them to vary at most 20%. Estimated from the detailed balance $k_{ba}/k_{ab} < e^{-\Delta E/RT}$ $=e^{-560/200}=6\%$, k_{ba} is at most 6% of k_{ab} . With all these constraints, the calculations show that $k_{ab}=23$ ps with input parameters,

$$k_a = 1/1.7 \text{ (ps}^{-1}); k_{bfast} = 1/4.5 \text{ (ps}^{-1});$$

 $k_{bslow} = 1/100 \text{ (ps}^{-1})k_{ab} = 1/23 \text{ (ps}^{-1});$
 $k_{ba} = 1/767 \text{ (ps}^{-1}),$

with prefactors of the subgroups and offset of the biexponential

$$A_{\text{fast}} = 0.22; \quad A_{\text{slow}} = 0.78; \quad \text{offset} = -0.075 \ 52.$$

Calculation results and experimental data are shown in Figs. 14(c) and 14(d). In the calculation itself, the uncertainty of $1/k_{ab}$ is smaller than 1 ps. The uncertainty of $1/k_{ab}$ mainly comes from experiments: the ion-bound and unbound ODs are overlapped with each other at 2635 cm⁻¹. Whenever the peak at 2635 cm⁻¹ is excited, a portion of the energy is absorbed by the unbound OD (<30%) which may not transfer its energy to CN. Counting for this factor, calculations show that the fastest OD to CN transfer time $1/k_{ab}$ is 17 ps. Therefore, the average OD to CN transfer time constant $1/k_{ab} = 20 \pm 3$ ps.

D. Comparison between a medium H-bond and a strong H-bond

In a previous system studied,³⁷ the coupling strength between the energy donor and accepter is 18 cm^{-1} with an energy mismatch of 97 cm⁻¹. The energy down-flow time constant is 330 ps. In the system studied here, the coupling strength is 200 cm⁻¹ with an energy mismatch of 560 cm⁻¹. The energy transfer time constant is 20 ps. Comparison between these two systems shows a qualitative correlation: a stronger coupling produces a faster energy transfer. The big energy mismatch does not show a significant effect on the OD to CN energy transfer rate. However, when the donor and acceptor are almost on resonance (mismatch of <30 cm⁻¹), the energy transfer time constants are fast, $\sim 20-40$ ps, even with a small coupling (probably <18 cm⁻¹).^{19,35} These observations raise an interesting question: how are the energy transfer rate, coupling strength, and energy mismatch correlated? In the following, we use an approximate equation derived from the Landau–Teller formula⁶¹⁻⁶⁵ to address this issue.

Within a fully quantum approach,⁶² the energy transfer rate from vibrational state i to state j can be described from the Fermi's golden rule as

$$k_{ij} = \gamma_{ij} \int_{-\infty}^{\infty} dt \, \exp(i\omega_{ij}t) \left\langle \frac{1}{2} \,\delta\beta(t), \delta\beta(0)_{+} \right\rangle,\tag{5}$$

where $\gamma_{ij} = 1/1 + \exp(-\hbar \omega_{ij}/kT)$ counts for the detailed balance. ω_{ij} is the energy difference. $\delta\beta(t)$ is a time dependent vibrational coupling between the two states as modulated by the bath. The expectation value can be replaced with a classical correlation function.⁶⁶ If we assume this correlation function to be a single exponential with a time constant τ_c , and further assume that τ_c is the spectral diffusion time (the assumption is reasonable to some extent, because the spectral diffusion time characterizes the evolution of solvent configurations and the fluctuation of vibrational coupling is largely caused by the molecular motions of the solvent), Eq. (5) can be rewritten as

$$k_{ij} = \gamma_{ij} \langle \delta \beta^2 \rangle \frac{\tau_c^{-1}}{\tau_c^{-2} + \omega_{ij}^2}.$$
 (6)

If we further assume that the fluctuation of vibrational coupling $\delta\beta$ is proportional to the average coupling strength $\langle\beta\rangle$, Eq. (6) becomes

$$k_{ij} = \gamma_{ij} y^2 \langle \beta \rangle^2 \frac{\tau_c^{-1}}{\tau_c^{-2} + \omega_{ij}^2},$$
(7)

where $y = \delta \beta / \langle \beta \rangle$. For simplicity, we assume y = 1. Now all parameters in the right part of Eq. (7) are experimentally accessible. Equation (7) has a similar form as what was used to calculate vibrational resonance energy transfer.^{30,31}

For the KSeCN/D₂O system, T=296 K, $\langle \beta \rangle$ =200 cm⁻¹, $\omega_{ij}=560$ cm⁻¹, and $\tau_c=1.9$ ps (time for 95% completion of the spectral diffusion). The energy transfer time constant from OD to CN is calculated to be $1/k_{\text{OD}\rightarrow\text{CN}}=16$ ps. The value is very close to 20 ps, which is experimentally determined. However, for the previous CDCl₃/C₆H₅SeCN system, T=296 K, $\langle \beta \rangle=18$ cm⁻¹, ω_{ij} =97 cm⁻¹, and $\tau_c=1.9$ ps. The calculated time constant is 90 ps, which is far from the measured value of 330 ps. There are a few plausible explanations for the inconsistency between the two systems. On the experimental side, among the four input parameters, T and ω_{ij} are precise. The determination of spectral diffusion times is straightforward. The systematic uncertainty of spectral diffusion time can be big (depending on its definition), but the relative uncertainty among systems is small. For example, the spectral diffusion times of both systems can be 3 ps (dependent on the definition), but it is not likely that one system is 1.9 ps while the other is 3 ps with the same analysis method. The three parameters in general can not induce such an inconsistency between the two systems.

Now the problem can be due to the coupling constant. The determination of the coupling constant requires many experimental parameters and one complicated model, which can cause a huge uncertainty of the coupling constant. Closely examining the parameters necessary for calculating the coupling constant for the CDCl₃/C₆H₅SeCN system, we found that the combinational anharmonicity of CD/CN is very small, only 6 ± 2 cm⁻¹, determined from two overlapped peaks. The value was obtained by simply subtracting peak positions which are actually shifted a little bit away from their original positions due to frequency overlap.³⁷ Counting for this small shift, $\Delta_{CD/CN} = 5\pm 2$ cm⁻¹. However, the refined value does not give a much different rate constant from 90 ps.

One possibility counting for the inconsistency remains. That is the preciseness of the model for calculating the coupling strength. Equation (2) comes from a perturbative limit: eigenvalues instead of values of local modes are used to calculate the "coupling between two normal modes"⁴⁶ (also see SI). Such assumptions will inevitably introduce some uncertainty into the final result. The uncertainty is dependent on the coupling constant. In the CDCl₃/C₆H₅SeCN system, the calculated coupling constant is less than 1% of the individual mode frequency (2155 and 2252 cm⁻¹). Such a small value can have a huge uncertainty because of the assumptions. Direct diagonalization of the model Hamiltonian matrix (given in the SI) can solve this problem. It can provide precise coupling constants between the energy donor and acceptor modes in the local mode basis. With the constraints of experimental data, the diagonalization of the refined gives $\beta_{OD/CN} = 175.5 \pm 0.5 \text{ cm}^{-1}$ matrix and $\beta_{\rm CD/CN}$ =9.7 \pm 0.2 cm⁻¹ (see SI). For the D₂O/SeCN⁻ system, this value (175.5 cm⁻¹) is only \sim 12% different from what (200 cm^{-1}) is obtained from Eq. (2). For the $CDCl_3/C_6H_5SeCN$ system, the difference is more than 40%. With values from the direct diagonalization, we obtain $1/k_{\text{OD}\rightarrow\text{CN}}=21$ ps and $1/k_{\text{CD}\rightarrow\text{CN}}=309$ ps from Eq. (7). Although now the two calculated time constants are very close to experimental data, we urge caution that it does not mean that Eq. (7) can precisely reproduce experimental results. Instead, it at most qualitatively shows that Eq. (7) can produce consistent results for two different systems. The calculated time constants strongly depend on what τ_c is in Eq. (7). Experimentally we do not have a precise way to define τ_c . There are two main reasons for us to choose $\tau_c = 1.9$ ps: one is that it is the turning point of the dynamic linewidth curve in Fig. 8(b), the other one is that 1.9 ps is the dissociation time of a H-bond with a dissociation enthalpy of 0.3-0.4 kcal/mol, which is close to the solvent reorganization energy

(activation energy for spectral diffusion).^{40,67,68} On the theoretical side, the assumptions we make in order to obtain Eq. (7) can be problematic. It is not clear how the spectral diffusion time is correlated with the vibrational coupling correlation time, especially when the spectral diffusion time is slow (in viscous liquids or solids). It is not clear either how the fluctuation of coupling strength is correlated with the strength itself. The correlations can be system dependent. Nonetheless, the results show that some simple equation like Eq. (7) has the potential to give some reasonable estimation for vibrational energy transfer rates.⁶⁹ We believe that with more experimental data available in the future, the equation should be able to be refined to the quantitative level.

In practice, an analytical equation similar to Eq. (7) which can provide reasonable estimations about energy transfer rates based on some easily accessible parameters will be extremely useful, even if it is empirical and at a very crude level. It will save researchers lots of time and resources in experimental designs (from our own experience).

IV. CONCLUDING REMARKS

Mode specific vibrational energy transfer from the OD stretch first excited state of D_2O to the first excited of CN stretch of SeCN⁻ is observed in a $D_2O/SeCN^- 2.5/1$ liquid mixture at room temperature. The coupling between the OD and CN stretches is determined to be 176 cm⁻¹, based on an exciton exchange model. The energy transfer time constant is determined to be 20 ± 3 ps, despite the big energy mismatch of -560 cm⁻¹ between the two modes. The energy transfer rate is substantially slower than the energy transfer between the ion-bound and unbound OD (<1.7 ps). With experimental determined parameters, an approximate analytical equation derived from the Landau—Teller formula qualitatively reproduces the energy transfer rates for two different systems.

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Figure S1. Feynman diagrams showing the origins of Peaks in fig. 1(B) and 1(C). R_1 and R_2 are for the Red peaks, and R_3 and R_4 are for the blue peaks. During the population period T_w , the excitation of one mode, e.g. CN, produces a hole on the ground state in R_1 and R_2 , and populations on the 1st excited state. The decay of the populations will fill the hole. Therefore, the peak pairs will decay with the vibrational lifetime of the population during the population period under the ideal situation.



Figure S2. Time dependent 2D IR spectra of a dilute (5%) HOD in $H_2O/NaBF_4$ (5.5 M) at 298 K.



Figure S3. Pump/probe data of a $D_2O/KSeCN 2.5/1$ mixture (A) and pure D_2O (B). In (A) the pump frequency is at 2635cm⁻¹, and in (B) it is 2550 cm⁻¹. In both samples, the photoproduct peaks appear at the same frequency 2685 cm⁻¹. It appears faster in D_2O because of the faster OD vibrational decay of the pure D_2O .



Figure S4. Vibrational (a) and rotational decays (b) from the 0-1 transition and (c) the 1-2 transition of the CN stretch of a 0.2 % KSeCN D₂O solution. The vibrational lifetime is 37 ps. The rotational time is 3.8 ± 0.3 ps (b) and 4.1 ± 0.2 ps (c).



Figure S5. Feynmann diagrams for mode-specific vibrational energy transfers induced ground state bleachings. In such a scenario, during the population period, the energy transfer from one mode to the other, e.g. from the 1st excited of OD to that of CN, inevitably induces the ground state bleaching of CN since some of CN has accepted energy from OD and leave the ground state to its 1st excited state.



Figure S6. Feynman diagrams showing the origins of mode-specific energy transfer from OD to CN blue cross peak (2635 cm⁻¹, 2042 cm⁻¹). The first interaction frequency (the x-coordinate in 2D IR spectra) ω_{01} is the OD 0-1 transition frequency 2635 cm⁻¹, and the emission frequency (the y-coordinate in 2D IR spectra) $\omega_{1'2'}$ is the CN 1-2 transition frequency 2042 cm⁻¹. During the population period, the excitation of OD stretch (11) transfers to CN (1'1'). The new created CN 1st excited state population (1'1') produces excited state absorption (1'2') and emits signal (180 degree out of phase with the probe beam) at the 1'-2' transition (CN 1-2) frequency. From the analysis, the growth of the cross peak is determined by the energy exchange rate, and the decay of the peak is determined by the CN vibrational relaxation.



Figure S7. Pump power dependent anisotropy decays of the CN stretch of a saturated KSeCN/D₂O solution from both 0-1 and 1-2 transitions. The inertial anisotropy values from the 0-1 transition with different pump power are almost identical ~0.35, and the rotational decay time constants are 4.7 ± 0.6 ps ($2.6 \ \mu J$), 4.5 ± 0.6 ps ($1.1 \ \mu J$), and 4.2 ± 0.6 ps ($0.4 \ \mu J$), respectively. The inertial anisotropy values from the 1-2 transition with three different pump powers are $0.21(2.6 \ \mu J)$, $0.24(1.1 \ \mu J)$, and $0.32(0.4 \ \mu J)$, respectively. The rotational decay time constants are 4.4 ± 0.6 ps ($2.6 \ \mu J$), 4.2 ± 0.6 ps ($1.1 \ \mu J$), and 4.0 ± 0.6 ps ($0.4 \ \mu J$), respectively. The rotational decay time constants are 4.4 ± 0.6 ps ($2.6 \ \mu J$), 4.2 ± 0.6 ps ($1.1 \ \mu J$), and 4.0 ± 0.6 ps ($0.4 \ \mu J$), respectively. The pump power dependent internal anisotropy values from the 1-2 transition are probably caused by either the saturation effect or high order nonlinear signal. At this point, we don't have any solid explanation for the obvious different inertial anisotropy values from both 0-1 and 1-2 transitions. The rotational time constants are within experimental uncertainty under different pump power, though the value seems to become smaller with lower pump power. The laser spot size on the sample is about 200 μm .



Figure S8. Waiting time dependent peak intensities with pump frequency at 2635 cm⁻¹. (a) waiting time up to 100 ps; and (b) waiting time up to 1 ns. Each contour represents 4% amplitude change.

The following derivation of eq (2) in the main text follows literature by Hamm and Hochstrasser¹. The equation (eq (2)) we obtain from the derivation is different from what was used by Rubtsov and Hochstrasser².



Figure. S9 Energy level diagram for a system of two oscillators. The isolated states (left side) are coupled by some weak interaction, which mixes them to generate the excitonic states (right side). Anharmonicity is introduced into this model by lowering the energies of the double excited monometric site states $|i_2 \rangle$ and $|j_2 \rangle$ by Δ from their harmonic energies $2\omega_i$. This anharmonicity mixes into all coupled states, giving rise to diagonal anharmonicity (Δ_{kk}) and off-diagonal anharmonicity (mix-mode anharmonicity, Δ_{kl}) in the basis of the normal modes discussed in the text.

The one exciton Hamiltonian H₁ mixes the monomeric site states |i> to create the oneexcitonic states $|v_k\rangle = \sum_i q_{ki} |i_1\rangle$ (see fig. S9). When the system is harmonic ($\Delta = 0$), the two-excitonic eigenstates of the two-excitonic Hamiltonian $H_2^{(0)}$ are simply Boson product states of the one-excitonic states: $\{a_{ij}(|v_k\rangle > |v_l\rangle + |v_l\rangle > |v_k\rangle)\}, l \leq k$, where the normalization factors are $a_{ii} = 1/2$ for l = k and $a_{ij} = 1/\sqrt{2}$ for $l \neq k$, respectively. The corresponding eigenvalues are $\omega_k + \omega_l$. The transformation matrix between the twoexciton basis and the site basis $\{a_{ii}(|i| > |j| > + |j| > |i| >)\}, i \leq j$, is

$$Q_{kl,ij} = 2a_{ij}a_{kl}(q_{ki}q_{lj} + q_{li}q_{ki})$$
(1)

Anharmonicity is introduced by reducing the site energies of only the double excited monomeric site states $|i\rangle|i\rangle$ by an energy Δ (see fig. S9). Δ_{kk} for k, and Δ_{ll} for l in the basis of the normal modes respectively. The perturbed Hamiltonian $H_2 = H_2^{(0)} + V$ consists of a harmonic part $H_2^{(0)}$ and an anharmonicity term V, which mixes the harmonic two excitonic states. The matrix elements of V in the site basis are: $V_{max} = -\Delta \delta_{ll} \delta_{ll} \delta_{ll}$ (2)

$$V_{ij,ij} = -\Delta \delta_{ij} \delta_{ij} \delta_{ij}$$

The matrix elements of V in the excitonic basis are:

$$V_{kl,mn} = -\sum_{ij} \Delta_{ij} Q_{kl,ij} \delta_{ij} Q_{ij,mn}^{-1} = -\sum_{i} \Delta_{ii} Q_{kl,ii} Q_{mn,ii} = -(\Delta_{kk} Q_{kl,kk} Q_{mn,kk} + \Delta_{ll} Q_{kl,ll} Q_{mn,ll})$$
(3)

The problem can then be evaluated assuming that the coupling is weak so that each oneexcitonic state is predominantly localized on an individual monomeric site:

$$q_{ij} = \delta_{ij} + q'_{ij} = \delta_{ij} + \frac{\beta_{ij}}{\omega_j - \omega_i}$$

$$\tag{4}$$

$$q_{ii} = q_{jj} = 1 \tag{5}$$

For off-diagonal anharmonicities:

$$\Delta_{kl} = V_{kl,kl} = -\sum_{i} \Delta_{ii} Q_{kl,ii} Q_{kl,ii} = -2\sum_{i} \Delta_{ii} q_{ki}^2 q_{li}^2 = -2(\Delta_{kk} + \Delta_{ll}) q_{kl}^2$$

$$= -2 \frac{(\Delta_{kk} + \Delta_{ll}) \beta_{kl}^2}{(\omega_k - \omega_l)^2}$$
(6)

 Δ_{kl} , Δ_{kk} , Δ_{ll} , ω_k and ω_l can be experimentally determined. Therefore, the coupling strength β_{kl} can be calculated directly from equation 6. From the notation, β_{kl} is the "coupling between two normal modes", which is different from β_{ij} in the basis of local mode. Under crude approximations, these two values can be considered to be the same.

We can analytically obtain β_{ij} and other parameters in the local mode basis, based on the experimentally determined eigenvalues and the diagonal and off-diagonal anharmonicities. From the energy level diagram in fig. S9, the total system Hamiltonian H for the coupled vibrations in the local mode basis is given by

$$H = \begin{bmatrix} 0 & 0 & 0 & 0 & \beta_{ij} & 0 \\ 0 & \omega_i & \beta_{ij} & 0 & 0 & 0 \\ 0 & \beta_{ij} & \omega_j & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\omega_i - \Delta_i & \sqrt{2}\beta_{ij} & 0 \\ \beta_{ij} & 0 & 0 & \sqrt{2}\beta_{ij} & \omega_i + \omega_j & \sqrt{2}\beta_{ij} \\ 0 & 0 & 0 & 0 & \sqrt{2}\beta_{ij} & 2\omega_j - \Delta_j \end{bmatrix}$$
(7)

Through the diagonlization of the matrix H, the corresponding eigenvalues (ω_k, ω_l) and the diagonal anharmonicities $(\Delta_{kk}, \Delta_{ll})$ and off-diagonal anharmonicities (Δ_{kl}) can be reproduced using the best-fit values of the parameters in the local Hamiltonian. The results are listed in Table S1 and S2.

Table S1. The input parameters and experimental data for the Hamiltonian matrix of C₆H₅SeCN and CDCl₃ system with $\Delta_{CD/CN} = 6 \pm 2 \ cm^{-1}$. When $\Delta_{CD/CN} = 5 \pm 2 \ cm^{-1}$, $\beta_{CD/CN} = 9.7 \pm 0.2 \ cm^{-1}$.

Input parameters	Experimental data
$\omega_i = 2156 \pm 1 cm^{-1}, \ \omega_j = 2251 \pm 1 cm^{-1}$	$\omega_k = 2155 cm^{-1}, \ \omega_l = 2252 cm^{-1}$
$eta_{ij} = 10.5 \pm 0.2 cm^{-1}$	$\beta_{kl} = 18 cm^{-1}$ (from eq.6)
$\Delta_i = 26 \pm 1 cm^{-1}, \ \Delta_j = 73 \pm 1 cm^{-1}$	$\Delta_{kk} = 25 cm^{-1}, \ \Delta_{ll} = 67 cm^{-1}$

Table S2. The input parameters and experimental data for the Hamiltonian matrix of KSeCN and D_2O system.

Input parameters	Experimental data
$\omega_i = 2137 \pm 1 cm^{-1}, \ \omega_j = 2574 \pm 1 cm^{-1}$	$\omega_k = 2075 cm^{-1}, \ \omega_l = 2635 cm^{-1}$
$eta_{ij} = 175.5 \pm 0.5 cm^{-1}$	$\beta_{kl} = 200 cm^{-1}$ (from eq.6)
$\Delta_i = 41 \pm 1 cm^{-1}, \ \Delta_j = 114 \pm 1 cm^{-1}$	$\Delta_{kk} = 33 cm^{-1}, \ \Delta_{ll} = 85 cm^{-1}$

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