

Mode-specific intermolecular vibrational energy transfer. I. Phenyl selenocyanate and deuterated chloroform mixture

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Vibrational energy transfer from the first excited state (2252 cm^{-1}) of the C–D stretch of deuterated chloroform (DCCl_3) to the 0-1 transition (2155 cm^{-1}) of the CN stretch of phenyl selenocyanate ($\text{C}_6\text{H}_5\text{SeCN}$) in their 1:1 liquid mixture was observed with a pump/probe two-color two dimensional infrared spectroscopic technique. The mode-specific energy transfer can occur mainly because of the long vibrational lifetime of the CN stretch first excited state ($\sim 300\text{ ps}$) and the relatively strong hydrogen-bond between the C–D and CN (calculated H-bond formation energy in gas phase $\sim -5.4\text{ kcal/mol}$). The mode-specific energy transfer is relatively low efficient (only $\sim 2\%$), which is mainly because of the relatively short vibrational lifetime ($\sim 9\text{ ps}$) of the C–D stretch first excited state and the big donor/acceptor energy mismatch (97 cm^{-1}) and the slow transfer kinetics ($1/k_{\text{CD-CN}} = 330\text{ ps}$). © 2010 American Institute of Physics.
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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. 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 vibration in a polyatomic solute can be monitored.^{6–8} Vibrational energy transfers from one mode to others are typically coupled together. The coupling makes it very difficult to experimentally investigate and analyze mode-specific energy transfer processes. This difficulty is especially salient in the intermolecular energy transfer processes, since most vibrational energy relaxations prefer intramolecular pathways because of stronger intramolecular couplings. Because of the difficulty, how the governing factors, e.g., coupling strength and energy mismatch, affect intermolecular 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 almost experimentally unexplored. There have been some findings about possible intermolecular mode-specific vibrational energy transfers.^{19,30,31} However, why these mode-specific energy transfers are effective is largely unknown.

Intermolecular vibrational energy transfer is a key part of many important phenomena, e.g., heat transportations and cell signaling. A molecular level understanding of these important processes inevitably requires knowledge about the

correction between intermolecular interactions and energy transfer dynamics. 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. We combined molecular designs and developing a high pump power version of two dimensional (2D) IR techniques to accomplish this goal. Our approach is to molecularly “decouple” two modes involved in the energy transfer process from other modes intramolecularly. This can be achieved by designing molecules based on the arguable “heavy atom effect.” Heavy atoms can arguably block intramolecular vibrational energy transfer from one mode to others in gas phase.^{32–34} In condensed phases, the phenomenon seems to also hold in some cases.^{35–37} We therefore chose and designed molecules with heavy atoms, e.g., Si, S, and Se, and measured vibrational lifetimes of these molecules. These heavy atoms were found indeed to be able to effectively block vibrational energy from relaxing to other modes inside the molecule in nonpolar solvents. For example, the CN stretch lifetimes of $\text{C}_2\text{H}_5\text{CH}_2\text{CN}$ ($\sim 2252\text{ cm}^{-1}$), $\text{C}_2\text{H}_5\text{SCN}$ ($\sim 2156\text{ cm}^{-1}$), and $\text{C}_2\text{H}_5\text{SeCN}$ ($\sim 2155\text{ cm}^{-1}$) in CCl_4 solutions are ~ 5.5 , ~ 84 , and $\sim 282\text{ ps}$ (see Fig. 1), respectively. The results clearly show that heavier atoms are better energy blockers ($\text{Se} > \text{S} > \text{C}$). In all nine RSeCN molecules we made, their CN lifetimes are all longer than 200 ps . However, the rule does not always hold, for instance, in CCl_4 solutions, the lifetime of Si–H of Cl_3SiH is 148 ps , while that of $(\text{C}_2\text{H}_5)_3\text{SiH}$ is only 6.3 ps which is even shorter than that of the CD stretch of CDCl_3 (see Fig. S1 in supporting materials). Nonetheless, by selectively designing molecules with heavy atoms, one should be able to get vibrational modes with lifetimes close or longer than 100 ps in condensed phases. Such long lifetimes are important to observe relatively inefficient intermolecular vibrational energy transfers.

Signals from intermolecular vibrational energy transfers

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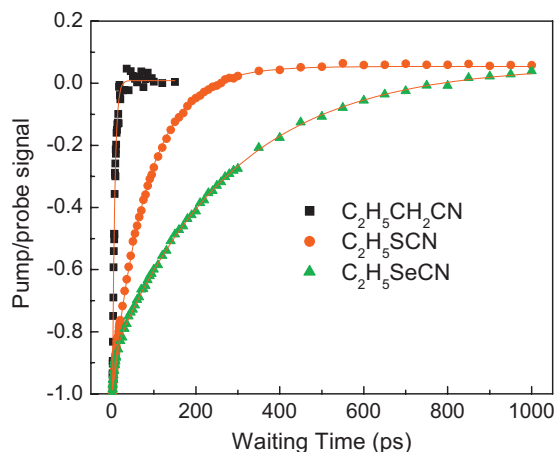


FIG. 1. Rotation-free pump/probe CN 1-2 transition data. Points are data. Lines are fits of $\text{C}_2\text{H}_5\text{CH}_2\text{CN}$ ($\sim 2252\text{ cm}^{-1}$), $\text{C}_2\text{H}_5\text{SCN}$ ($\sim 2156\text{ cm}^{-1}$), and $\text{C}_2\text{H}_5\text{SeCN}$ ($\sim 2155\text{ cm}^{-1}$). Lifetime of $\text{C}_2\text{H}_5\text{CH}_2\text{CN}$ is 5.5 ps. Lifetime of $\text{C}_2\text{H}_5\text{SCN}$ is 84 ps. Lifetime of $\text{C}_2\text{H}_5\text{SeCN}$ is a biexponential: $\sim 13\%$ at 5.7 ps, and the rest 87% at 282 ps.

can be very weak due to their slow kinetics. In addition, precise analysis of energy transfer kinetics requires many data points which can be very time consuming to acquire. We recently demonstrated that an intermolecular vibrational energy transfer could be monitored with an echo 2D IR technique.³¹ However, for general investigations of intermolecular vibrational energy transfers, current 2D IR techniques^{38–51} can have some difficulties because of either their low pump powers or their slow data acquisition rates. Therefore, we built a high pump power version of two-color 2D IR setup, which is based on the synchronization of one picosecond amplifier and one femtosecond amplifier. The setup allows us to tune the pump and probe frequencies independently in a very wide range. It also allows us to probe vibrational modes with very weak transition dipole moments because of its high pump power (up to $40\text{ }\mu\text{J/pulse}$ with a bandwidth $\sim 21\text{ cm}^{-1}$) which is more than ten times higher than one can get from the étalon method.²⁶

In this paper, we will describe our first mode-specific intermolecular vibrational energy transfer experiment. The system studied is a $\text{C}_6\text{H}_5\text{SeCN}/\text{DCCl}_3$ liquid mixture with a molar ratio 1:1. Vibrational energy transfer from the first excited state (2252 cm^{-1}) of the C–D stretch of deuterated chloroform (DCCl_3) to the 0-1 transition (2155 cm^{-1}) of the CN stretch of phenyl selenocyanate ($\text{C}_6\text{H}_5\text{SeCN}$) in the mixture was observed with the pump/probe two-color 2D IR technique.

II. EXPERIMENTS

The optical setup can be briefly described as follows. A picosecond amplifier and a femtosecond amplifier are synchronized with the same seed pulse. The picosecond amplifier pumps an optical parametric amplifier (OPA) to produce $\sim 1\text{ ps}$ mid-IR pulses with bandwidth $\sim 21\text{ cm}^{-1}$ (variable from 14 to 26 cm^{-1}) in a tunable frequency range from 900 to 4000 cm^{-1} with energy $10\text{--}40\text{ }\mu\text{J/pulse}$ at 1 KHz . The femtosecond amplifier pumps another OPA to produce $\sim 140\text{ fs}$ mid-IR pulses with bandwidth $\sim 200\text{ cm}^{-1}$ in a

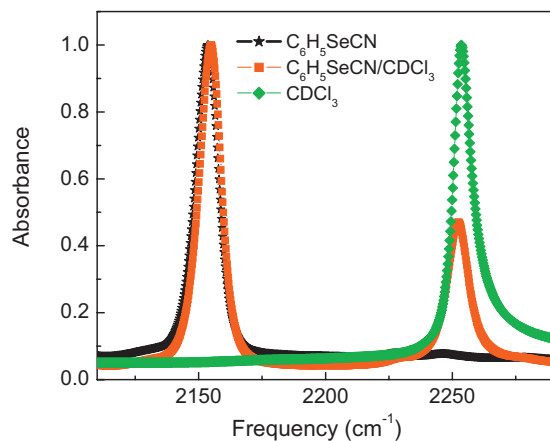


FIG. 2. FTIR spectra of pure $\text{C}_6\text{H}_5\text{SeCN}$ liquid, pure DCCl_3 , and their mixture with a molar ratio 1:1. The peak at 2155 cm^{-1} is the CN stretch mode of the $\text{C}_6\text{H}_5\text{SeCN}$ molecule, and the peak at 2252 cm^{-1} is the CD stretch mode of the DCCl_3 molecule.

tunable frequency range from 900 to 4000 cm^{-1} with energy $10\text{--}40\text{ }\mu\text{J/pulse}$ 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.⁵² Vibrational lifetimes are obtained from the rotation-free 1-2 transition signal $P_{\text{life}} = P_{\parallel} + 2 \times P_{\perp}$, where $P_{\parallel}$ and $P_{\perp}$ are parallel and perpendicular data, respectively. Rotational relaxation times are acquired from $\tau = P_{\parallel} - P_{\perp} / P_{\parallel} + 2 \times P_{\perp}$.

Most chemicals were purchased from Aldrich and used as received. The RSeCN compounds were synthesized based on literature.⁵³ Temperature dependent 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.⁵⁴ The DFT calculations were carried out as implemented in the GAUSSIAN98 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. Linear FTIR spectra

Figure 2 displays the FTIR spectra of $\text{C}_6\text{H}_5\text{SeCN}/\text{DCCl}_3$ liquid samples. The CD and CN stretch frequencies are 2252 and 2155 cm^{-1} , respectively. The H-bond between the two groups only shifts their frequencies for $\sim 1.5\text{ cm}^{-1}$. DFT calculations show that the two molecules form two possible H-bonds [Figs. 3(a) and 3(b)]. The H-bond [Fig. 3(a)] between CD and CN (formation energy -5.36 Kcal/mol) is more stable than the one [Fig. 3(b)] between CD and CH (formation energy -3.83 kcal/mol). The

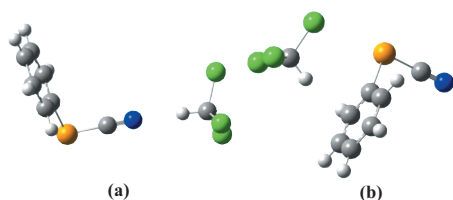


FIG. 3. Two calculated H-bonds between $\text{C}_6\text{H}_5\text{SeCN}$ and DCCl_3 in gas phase. (a) is more stable than (b) by ~ 1.53 kcal/mol.

formation energy of the stable H-bond is about two times of the calculated value of H-bond between phenol and benzene.⁵⁵ The calculated value and the fact that CN is a much better H-bond acceptor than Cl of Chloroform suggests that at room temperature (RT) in a $\text{C}_6\text{H}_5\text{SeCN}/\text{DCCl}_3$ 1:1 mixture, most of the molecules form H-bonded pairs.

B. 2D IR spectra

The relative strong interaction between CD and CN, and the long vibrational lifetime of CN (~ 330 ps), give us some confidence that we may be able to observe vibrational energy transfer between the two modes on the two molecules. 2D IR measurements (Fig. 4) do show vibrational energy can transfer from CD to CN. In addition, two observations are somehow out of our expectations. First, the apparent transfer efficiency is very low, only $\sim 2\%$, and the transfer kinetics is much slower than what we would expect. Second, the up-pumping transfer from CN to CD seems to be very slow that it can hardly be observed.

Figure 4 Displays waiting time dependent 2D IR spectra and an energy level diagram showing the peak origins in the spectra of a $\text{C}_6\text{H}_5\text{SeCN}/\text{Cl}_3\text{CD}$ (1/1 molar ratio) mixed liquid at room temperature. Peak decays and growth in the 2D IR spectra [Fig. 4(a)] indicate how vibrational energies of CD and CN decay and transfers between the two molecules. In the following, we will describe in details how each peak grows in the spectra.

At short waiting times, e.g., 1 ps, two red/blue peak pairs show up in the spectrum [Fig. 4(a) panel 1 ps]. One pair belongs to the CD stretch, and the other belongs to the CN stretch. Peak 1 is the CD 0-1 transition, and peak 2 is its 1-2 transition. The blue peak shifts to a lower frequency along the probe axis because of the anharmonicity of molecular vibrations. The anharmonicity can be directly read out from the position difference (67 cm^{-1}) along the probe axis between the two peaks. Peak 3 is the CN 0-1 transition, and peak 4 is its 1-2 transition. Its vibrational anharmonicity is 25 cm^{-1} . From Fig. 4(a), we can see that the CD peak pair decays much faster than the CN peaks. This is because the vibrational lifetime of the CN stretch (~ 330 ps) is much longer than that of the CD stretch (~ 8.6 ps). In addition, we can also see some peaks grow in on the off-diagonal positions, e.g., peaks 5, 6, 7, 8, and 9. The growth of these cross peaks is one major feature of 2D IR spectra, which can be utilized to analyze detailed molecular structures and dynamics. It is similar to the appearances of cross peaks in multiple-dimensional NMR.⁵⁶ In general, several molecular phenomena can induce such a cross-peak appearance: vibrational coupling,^{42,57,58} intramolecular vibrational energy

transfers,^{29,48,57,59} intermolecular vibrational energy and heat transfers,³¹ and molecular transformations.^{50,59,60}

In the sample studied, the two vibrations CD and CN belong to two different molecules. They cannot chemically interconvert into each other. Therefore, the molecular phenomena responsible for the growth of the cross peaks in Fig. 4(a) must be intermolecular vibrational energy and heat transfers [At short T_w s, some very weak cross peaks due to the CD/CN coupling already appear. They do not show up in Fig. 4(a) because their amplitudes are smaller than 1% of the maximum peak. See Fig. S2 in supporting materials. From the coupling peaks and a simple exciton model,⁶¹ the coupling between the CD stretch and the CN stretch is 19 cm^{-1}]. Similar cross-peak growths have been observed in a $\text{CD}_3\text{CN}/\text{C}_6\text{H}_5\text{CN}$ mixture where vibrational energy does not transfer between the two CN groups which are simply the probes of energy transfers among other modes.³¹ In the $\text{C}_6\text{H}_5\text{SeCN}/\text{Cl}_3\text{CD}$ mixture studied in this work, situation is different. The cross peaks are caused by heat and mode-specific vibrational energy transfer from CD to CN. Experimental facts and theoretical explanations to support this conclusion are presented in next paragraphs.

The red cross peak 8 is caused by the CD absorption transparency induced by heat from the vibrational relaxation of CN and the possible direct vibrational energy transfer from CN to CD. The physical picture for the heat induced growth of this peak is stated as following. Following the relaxation of some vibrational energy of CN into heat, the sample is heated up. The absorption cross section of CD decreases with the increase of temperature (see temperature dependent FTIR spectra in supporting materials Figs. S3 and S4), which is the heat inducing transparency.⁶² The peak's pump frequency is 2155 cm^{-1} , representing the heat coming from the CN 0-1 transition relaxation. Its probe frequency is 2252 cm^{-1} , representing the signal coming from the CD stretch. The Feynman Diagrams describing the light/material interaction origin for this peak are provided in the supporting materials (Fig. S5). Peak 8 is also possibly from the mode-specific vibrational energy transfer from CN to CD. However, very little blue cross peak 10 at (2155 and 2185 cm^{-1}) observed means that the contribution to the overall intensity peak 8 of this possibility is very small.

Since the heat for this peak is from the relaxation of the CN stretch, we would expect that the growing kinetics of this peak should resemble to the decay dynamics of the CN stretch after the vibrational relaxation/heat conversion equilibrates. In a molecule, the typical equilibration time for the intramolecular vibrational energy to relax into heat is $100\text{--}200\text{ ps}$.^{4,6,31,63} Because of the blocking effect of Se, the vibrational lifetime of CN is about 330 ps in the sample mixture. The rest of the parts of the molecule $\text{C}_6\text{H}_5\text{SeCN}$ are only composed of C and H, which we would expect to have a similar vibrational dynamic behavior as most molecules observed. Therefore, before the vibration/heat equilibration ($100\text{--}200\text{ ps}$) of the other parts of the molecule, the CN relaxation is always faster than the heat generation. After the equilibration, heat generation should be almost synchronized with the CN relaxation. This is exactly what we observed from the growth of peak 8 and the decay of the CN 1-2

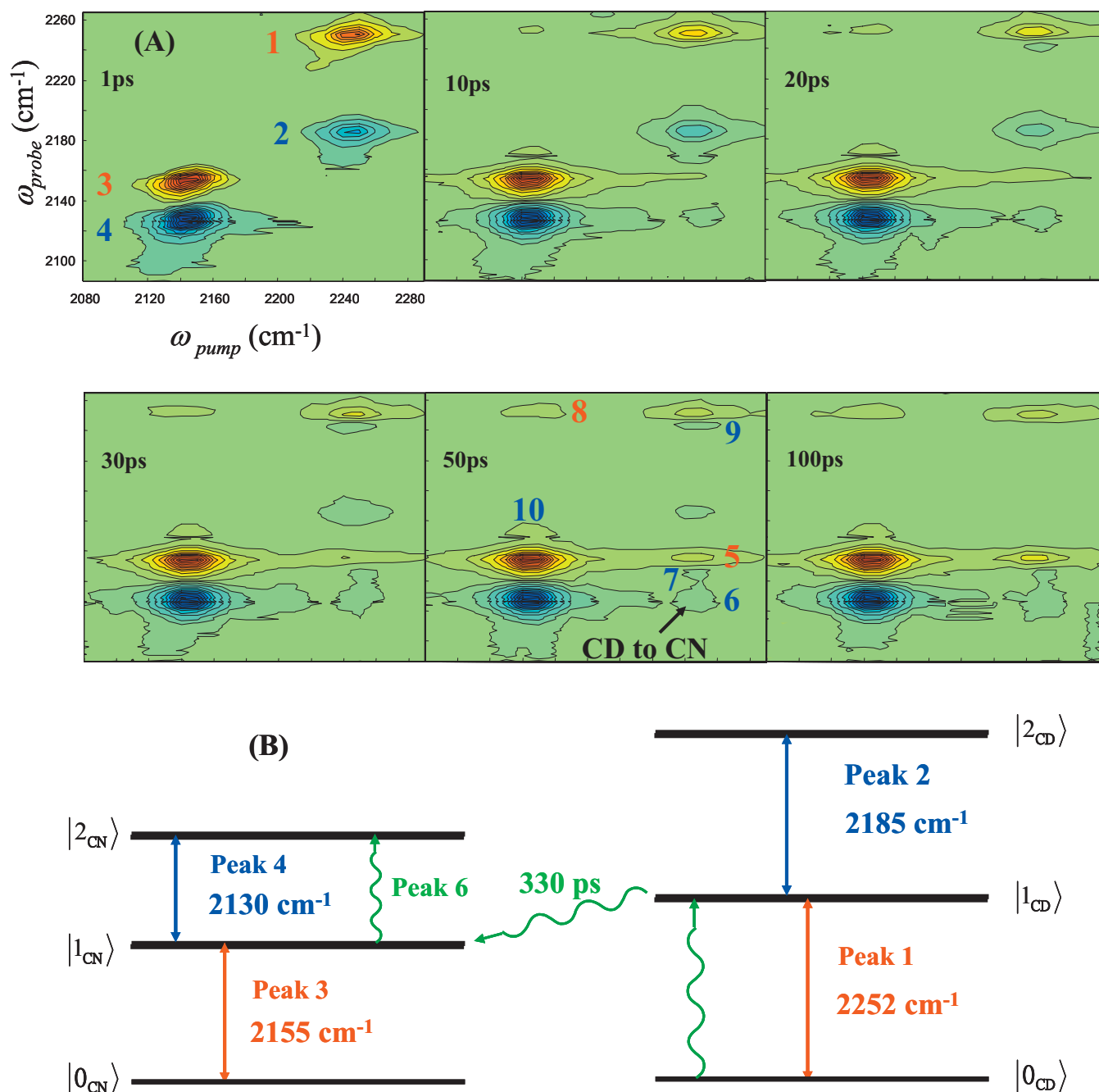


FIG. 4. Waiting time dependent 2D IR spectra and peak intensities of a $\text{C}_6\text{H}_5\text{SeCN}/\text{Cl}_3\text{CD}$ (1/1 molar ratio) mixed liquid at room temperature. (a) 2D IR spectra showing how peaks grow in or decay due to vibrational energy relaxations and transfers. (b) Energy level diagram showing the origins of peaks 1, 2, 3, 4, and 6. The wavy curves demonstrate how energy flows from CD to CN to produce the energy transfer peak 6. In 2D IR spectra, each contour represents 10% intensity increase except the smallest two (5% and 1% of the maximum intensity, respectively). In the 1 ps panel, the smallest contour is 5%.

transition peak 4, as shown in Fig. 5. According to literature,^{6,64} the pump power on the sample, the absorption and path length of the sample, and the focus size of the laser, the temperature is increased about 5–10 °C locally.

Blue cross peak 6 is from the mode-specific vibrational energy transfer from CD to CN. Its pump frequency is at 2252 cm⁻¹, representing that the energy is from the CD 0-1 transition. Its probe frequency is at 2130 cm⁻¹, representing that the signal is from the CN 1-2 transition, which indicates the existence of the CN first state population. Since this CN first excited state population is not from direct laser excitation (diagonal peak pairs are from direct laser excitations), it

must come from direct energy transfer from the CD stretch 0-1 excitation. Feynman Diagrams describing the light/material interaction origin for this peak are provided in the supporting materials (Fig. S6). Two other molecular processes can also produce cross blue peaks at positions close to peak 6: intermolecular heat induced absorption and vibrational relaxation induced combination band absorption.^{29,31,59} Typically these two processes induce a relatively small frequency shifts from the cross red peak. We can see such an effect from the 2D IR spectra. From panel 20–100 ps, we can clearly see that a blue peak 7 grows.

The red cross peak 5 has several origins: heat induced

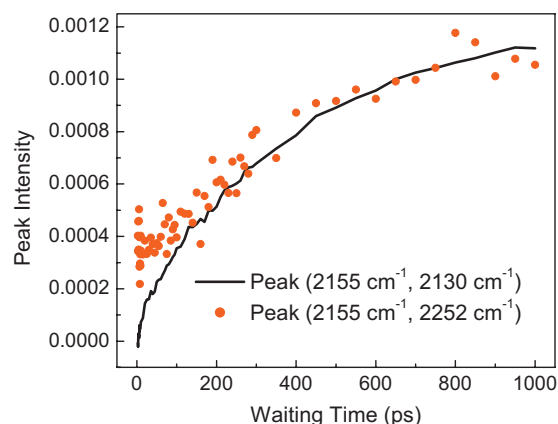


FIG. 5. Waiting time dependent peaks 8 (dots) and 4 (line) intensities. The intensities of peak 4 are rescaled and its sign is flipped to match those of peak 8. Before 200 ps, the growth of peak 8 is slower than the decay of peak 4 because it takes time for those modes accepting energy from CN to convert their energy into heat. After 200 ps, the kinetics is similar, because the equilibration is much faster than the CN relaxation. Therefore, the heat generation and CN relaxation are almost synchronized.

transparency and possible vibrational relaxation induced ground state bleaching,³¹ and the mode-specific vibrational energy transfer from CD to CN. Two of the origins can be experimentally confirmed. Heat induced transparency can be justified by the temperature dependent FTIR spectra (see supporting materials). The mode-specific vibrational energy transfer from CD to CN is confirmed by the appearance of the blue cross peak 6. According to theory, there must be a 0-1 transition peak 5, corresponding to the 1-2 transition peak 6 induced by the energy transfer (see Figs. S5 and S6 in the supporting materials). The vibrational relaxation induced ground state bleaching is difficult to experimentally justify since the vibrational lifetime of CN is longer than 300 ps and the diagonal CN peaks 3 and 4 do not show clear frequency shifts with time. All these contributions add up together making its amplitude bigger than any cross blue peak underneath of it.

A small blue peak 9 grows in and then disappears just underneath of the CD 0-1 transition red peak in the 2D IR spectra. This peak is a typical intramolecular vibrational relaxation induced combination band absorption, which has been observed in many systems with pump/probe and 2D IR methods.^{19,29,31,59,65} The origin of this peak can be stated as the following: The excitation of CD stretch relaxes to other modes which are strongly coupled to the CD stretch inside the molecule. While these modes are excited through accepting the energy from the CD stretch, they form a new combination band with the CD stretch 0-1 transition. Light at the combination band frequency (a little lower than the CD 0-1 transition) is then absorbed by this new band. Feynman Diagrams describing the light/material interaction origin for this peak are provided in the supporting materials (Fig. S7).

C. Kinetic analysis of energy transfer from CD to CN

The appearance and growth of the blue cross peak 6 confirm mode-specific vibrational energy transfer from CD

to CN. The energy transfer efficiency is somehow unexpectedly low, only $\sim 2\%$, indicating relatively slow energy transfer kinetics from CD to CN.

Before we analyze the energy transfer kinetics, one issue must be resolved: Does the formation and dissociation dynamics of H-bond between CDCl_3 and $\text{C}_6\text{H}_5\text{SeCN}$ in the sample affect the vibrational energy transfer kinetics between CD and CN? It is now clear that H-bonds dissociate and form in RT liquids at picosecond time scales (10^{-11} – 10^{-9} s).³⁷ These time scales overlap with those of vibrational energy transfers. It seems that vibrational energy transfer kinetics must be affected by the H-bond dynamics. This conclusion is true for systems with several exchangeable H-bonded or free species whose energy transfer kinetics are different. In the system we studied, most molecules in the system are always H-bonded due to their big formation energy [based on the calculated $\Delta E = -5.36$ (kcal/mol)], even though the detailed partners of a H-bond are always changing. In other words, we always have only one major H-bond state in the system. Therefore, most of the vibrational energy transfers occur when two molecules are H-bonded. Because of this, the system can be treated as “static” H-bonded pairs for the energy transfer kinetics analysis. This is a similar reasoning as that pure liquids can be used to study vibrational relaxations without worrying about the resonant energy transfers among the molecules of the same species.⁶

Another concern is what will happen if the H-bond is very weak (the calculated H-bond energy is far off) or some non-H-bonded species are competing, e.g., complexes with Cl of CDCl_3 pointing to the benzene ring of $\text{C}_6\text{H}_5\text{SeCN}$, so that a significant part of the molecules are not H-bonded, e.g., 10%–20% (the CN group is a much better H-bond acceptor than Cl, this assumed value is already much bigger than it should be). This situation occurs when the effective H-bond binding energy is smaller than 1.8 kcal/mol (RT). Our previous experiments have shown that this type of H-bonds will dissociate and reform within a few picoseconds,³⁷ which is much faster than the energy transfer studied here. In addition, the transition dipole moment of the free CD is much smaller than the bonded one, which makes sure that the signal observed is mainly from the bonded species. Therefore, the effect of the H-bond dynamics is simply to change the apparent population of the CD excitation, which is incorporated in the apparent vibrational decay. In this system, because the bonded and free species (if any) are spectrally overlapped, the measured energy transfer rate is the average rate of both free and bonded species. However, since most molecules are bonded and the transfer rate is much faster when bonded, the measured rate is still mainly for the bonded species.

To analyze the mode-specific energy transfer kinetics, we construct a simple model, where CD and CN can exchange vibrational energy, and they also decays with their own lifetimes and possible H-bond dynamics. The model can be illustrated in the following scheme:

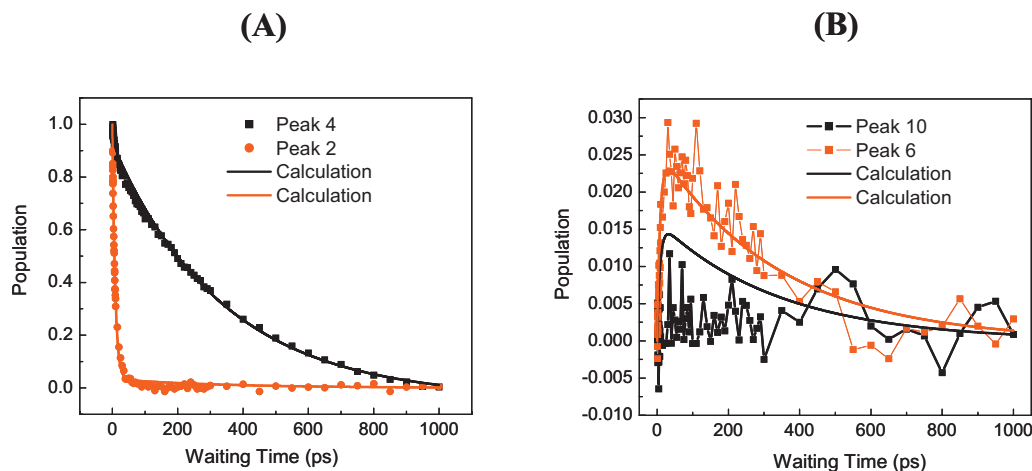


FIG. 6. Intensities of peaks 2, 4, 6, and 10 in Fig. 4(a) and calculations based on the biexponential model. The CD to CN vibrational energy transfer time constant is 330 ps. The up-pumping energy transfer from CN to CD is slower. Its time constant is 532 ps. The results are within calculation uncertainties of the single exponential model calculations.



where k_a and k_b are the vibrational lifetimes of CD and CN, respectively, and k_{ab} and k_{ba} are the energy exchange rate constants. In experiments, we can obtain rotation-free data. Therefore, the model does not include any rotational components. In the model, the time dependent CD and CN populations are provided by the normalized intensities of the CD 1-2 peak 2, CD to CN cross peak 6, CN 1-2 peak 4, and assumed CN to CD peak 10. The normalization of the CD to CN cross peak population is obtained by dividing its intensity by the square root of the intensity ratio ($I_{\text{CN}}/I_{\text{CD}}=2.5$) of the CN and CD diagonal peaks at 1 ps. The normalization of the CN to CD peak is to multiple the same constant. The normalization is to compensate for difference between transition dipole moments of CD and CN.

None of the four parameters, k_a , k_b , k_{ab} , and k_{ba} , is known beforehand. This is different from chemical exchange experiments.^{37,50,55} The vibrational lifetimes of the CD and CN cannot be predetermined in their pure liquids, because different solvents can change the lifetimes substantially. In pure CDCl_3 , the lifetime of CD stretch is ~ 15.7 ps (data in supporting materials Fig. S8), while its apparent lifetime in the $\text{CDCl}_3/\text{C}_6\text{H}_5\text{SeCN}$ 1:1 mixture is only 8.6 ps. The shorter lifetime in mixture is not caused by the vibrational energy transfer from CDCl_3 to $\text{C}_6\text{H}_5\text{SeCN}$, but mainly the environmental change, which causes the intramolecular relaxation of CDCl_3 faster, as we can see from the following data analysis. In the $\text{CDCl}_3/\text{C}_6\text{H}_5\text{SeCN}$ 1:1 mixture, the CN stretch decays slower than in its pure liquid in the initial period (~ 200 ps), and then it decays faster than in its pure liquid after 200 ps (see supporting materials). k_{ab} and k_{ba} are energy exchange rate constants to be obtained from the calculations.

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 CD and CN in the mixture

must be very close to their apparent lifetimes [the rotation-free decay time constants of their 1-2 transition peaks in Fig. 4(a)], because the vibrational energy involved in the mode-specific vibrational exchange is only $\sim 2\%$ of the initial excitation energy. (Here, we assume that CD or CN is the best intermolecular energy acceptor for each other in the system, since no other modes with visible intensities are within the frequency range.) Therefore, in calculating the data, we used $k_a=8.6$ ps and $k_b=330$ ps (their apparent lifetimes) as initial input values and allowed them to vary at most 20%. From experimental data and theory by Kenkre *et al.*⁹ or the detailed balance, we also know that $k_{ba}=0.62k_{ab}$. With all these constraints, the calculation yields $1/k_{ab}=320$ ps.

The calculations fit experimental results reasonably well, but it obviously misses the early intensity decay part of peak 4. This is because the apparent vibrational lifetime of CN is not a rigorous signal exponential, but a biexponential with $\sim 10\%$ fast component of ~ 12 ps and $\sim 90\%$ slow component of ~ 400 ps in the mixture. Therefore, we constructed another kinetic model to analyze the data, based on this CN biexponential lifetime. The core of the new model is identical to Eq. (1). The only difference is that we separate the $\text{C}_6\text{H}_5\text{SeCN}$ into two subgroups. The weighing of each subgroup is determined by the prefactors of the biexponential. Each subgroup has a single-exponential-decay lifetime time. Each can exchange energy with CD, but the subgroups cannot exchange energy with each other (this follows the assumed physical picture of biexponential: the subcomponents can be considered as independent species). Following this new model, calculations fit experimental results much better, as shown in Fig. 6. The calculation parameters are $k_a=1/8.6(\text{ps}^{-1})$; $k_{\text{bfast}}=1/11.5(\text{ps}^{-1})$; $k_{\text{bslow}}=1/900(\text{ps}^{-1})$; $k_{ab}=1/330(\text{ps}^{-1})$; and $k_{ba}=1/532(\text{ps}^{-1})$ with prefactors of the subgroups and offset of the biexponential $A_{\text{fast}}=0.09$; $A_{\text{slow}}=0.91$; and offset $=-0.04$.

The biexponential model yields energy transfer time constants $1/k_{\text{CD} \rightarrow \text{CN}}=330$ ps and $1/k_{\text{CN} \rightarrow \text{CD}}=532$ ps (required by the detailed balance). These values are very close to those obtained from the single exponential calculations. The similarity derives from the fact that energy exchange

rates are very sensitive to the intensity growth of the energy exchange peaks, while they are not very sensitive to minor changes of vibrational lifetimes of each species.

In Fig. 6(b), the calculated intensity of peak 10 (black curve) is obviously bigger than the experimental value (black dots). There may be three possibilities which can cause such an observation: (1) the detailed balance breaks down so that the energy up-pumping from CN to CD is much slower than the down-flow rate; (2) the kinetic model is oversimplified; and (3) the intensity of peak 10 is so small that it is within experimental uncertainty. The first possibility (breakdown of the detailed balance) is very unlikely, since the microscopic reversibility holds for the energy forward and backward transfer processes. One exception may “break” (not real breakdown) the reversibility is that the energy flowing-down requires one special complex and solvent configuration, while the energy pumping-up process requires another configuration. Under this situation, the energy flowing-down and pumping-up processes can be considered independent. However, the explanation is only suitable for very fast pumping-up processes (faster than predicted by the detailed balance) but not for the slow processes, since the molecules in the mixture rotate much faster than the energy transfers so that they can always find the optimum configuration to transfer energy. The second possibility is also unlikely. The kinetic model can be oversimplified about how many H-bonded or unbonded species. However, this simplification does not change the detail balance. What it affects are the transfer rate constants and what species the rate constants are from. The third possibility is most likely. Peaks 2, 4, and 6 fit the model calculation very well with the assumption of detailed balance (Fig. 6). Only peak 10 deviates from the calculation, which can imply that the model can be reasonable but the experimental data of peak 10 can be problematic. Different from peak 6, peak 10 is very close to peak 3 which has a signal more than 160 times bigger with an opposite sign. The cancellation effect of peak 3 makes peak 10 hardly observable (see Fig. S11).

IV. PERSPECTIVE

Previous results show that intermolecular vibrational energy transfers among some experimentally undefined modes can occur at 20–40 ps,^{19,31} which is almost ten times faster than what we observed. It would be interesting to compare those systems and the system studied here. The previous studied systems are CDBr₃/CHBr₃ mixture¹⁹ and CD₃CN/C₆H₅CN mixture.³¹ In either system, the intermolecular interaction is smaller than the H-bond in the system studied in this work. It would be reasonable to assume that the coupling strength between CD and CN in our system (19 cm⁻¹) to be stronger than either case studied before. According to theory,⁹ the only reason for those systems to be faster than our system is that they have a much smaller energy mismatch or a very different photon density distribution (less likely). In those two systems, energy transfer modes are quasiresonant, e.g., the energy mismatch between two energy transfer modes in the CDBr₃/CHBr₃ mixture is ~20 cm⁻¹. According to calculations (in supporting materials Fig. S9),

the energy transfer rate with a 20 cm⁻¹ energy mismatch is 4–14 times (depending on the density of states used) bigger than the rate with a 97 cm⁻¹ energy mismatch, providing the same coupling strength and phonon density. The rate constant for our system with a 97 cm⁻¹ energy mismatch is 330 ps, while the rate constant for the CDBr₃/CHBr₃ mixture with a 20 cm⁻¹ energy mismatch is 25 ps.¹⁹ The ratio is 14 times. This experimental value is qualitatively consistent with the theoretical predictions.

The simple comparison between theoretical calculations and experiments points out the important effects of energy mismatch and coupling strength on intermolecular vibrational energy transfer kinetics.⁶⁶ In future experiments, we will focus on investigating the effects of these two factors with tunable energy mismatch gaps and interaction strengths.

V. CONCLUDING REMARKS

A mode-specific intermolecular vibrational energy transfer with an energy mismatch 97 cm⁻¹ is observed. Despite the relatively strong interaction between the energy donor (CD) and acceptor (CN), the energy transfer efficiency is low, only ~2%. The low efficiency is due to the short vibrational lifetime of the donor (~9 ps) and the slow energy transfer rate (~330 ps). The slow transfer rate is partially caused by the big energy mismatch.

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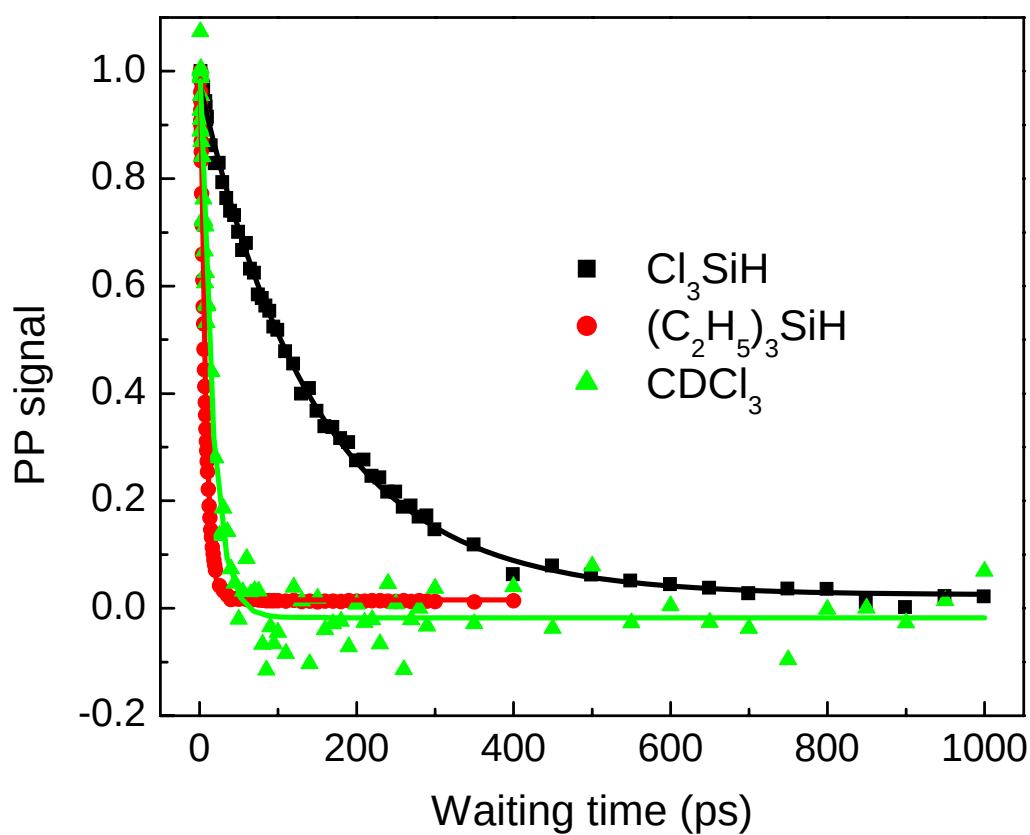


Figure S1. Rotation-free pump/probe data of SH stretches of Cl_3SiH and $(\text{C}_2\text{H}_5)_3\text{SiH}$ in CCl_4 solutions, and CD stretch of CDCl_3 in bulk liquid. The vibrational lifetimes are 148 ps (Cl_3SiH), 6.3 ps ($(\text{C}_2\text{H}_5)_3\text{SiH}$), and 15.7 ps (CDCl_3), respectively.

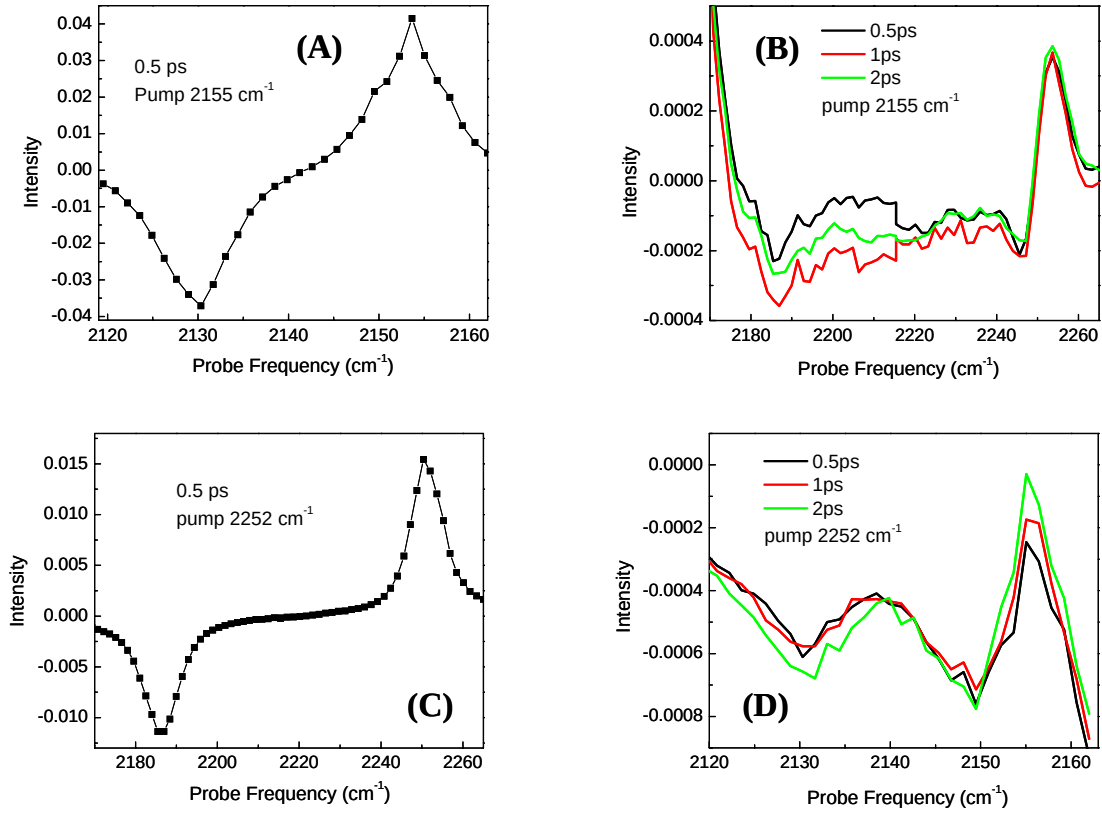


Figure S2. Spectra of perpendicular polarization showing intensities of diagonal and cross peaks at short T_w s. (A) Spectrum at $T_w = 0.5$ ps, pumped at 2155 cm⁻¹. The peaks in (A) correspond to Peak (2155 cm⁻¹, 2155 cm⁻¹) and Peak (2155 cm⁻¹, 2130 cm⁻¹) in Fig. 4(A) in the main text. (B) Spectra at $T_w = 0.5$ ps, 1 ps, 2 ps, pumped at 2155 cm⁻¹. The peaks in (B) correspond to Peak (2155 cm⁻¹, 2252 cm⁻¹), Peak (2155 cm⁻¹, 2246 cm⁻¹) and Peak (2155 cm⁻¹, 2185 cm⁻¹) in Fig. 4(A) in the main text. The small peak (2155 cm⁻¹, 2185 cm⁻¹) is the CD 1-2 transition due to the direct laser excitation of CD from the tail of the laser spectrum. It decays with the lifetime of the CD stretch. Most of Peak (2155 cm⁻¹, 2252 cm⁻¹) and Peak (2155 cm⁻¹, 2246 cm⁻¹) are the combination band peaks of CD and CN. The combination band anharmonicity is 6 ± 2 cm⁻¹. (C) Spectrum at $T_w = 0.5$ ps, pumped at 2252 cm⁻¹. The peaks in (C) correspond to Peak (2252 cm⁻¹, 2252 cm⁻¹) and Peak (2252 cm⁻¹, 2185 cm⁻¹) in Fig. 4(A) in the main text. (D) Spectra at $T_w = 0.5$ ps, 1 ps, 2 ps, pumped at 2252 cm⁻¹. The peaks in (D) correspond to Peak (2252 cm⁻¹, 2155 cm⁻¹), Peak (2252 cm⁻¹, 2149 cm⁻¹) and Peak (2252 cm⁻¹, 2130 cm⁻¹) in Fig. 4(A) in the main text. The small peak (2252 cm⁻¹, 2130 cm⁻¹) at 0.5 ps is the CN 1-2 transition due to the direct laser excitation of CN from the tail of the laser spectrum. It decays with the lifetime of the CN stretch. Most of Peak (2252 cm⁻¹, 2155 cm⁻¹) and Peak (2252 cm⁻¹, 2149 cm⁻¹) are the combination band peaks of CD and CN. The combination band anharmonicity is 6 ± 2 cm⁻¹. The amplitudes of the cross peaks are less than 1% of the maximum diagonal peak as shown in the plots. In addition, at 2 ps, energy already begins

to transfer from CD to CN (the growths of peaks(2252 cm^{-1} , 2130 cm^{-1}) and (2252 cm^{-1} , 2155 cm^{-1}) in (D)), but no transfer from CN to CD (no peak growths in (B)).

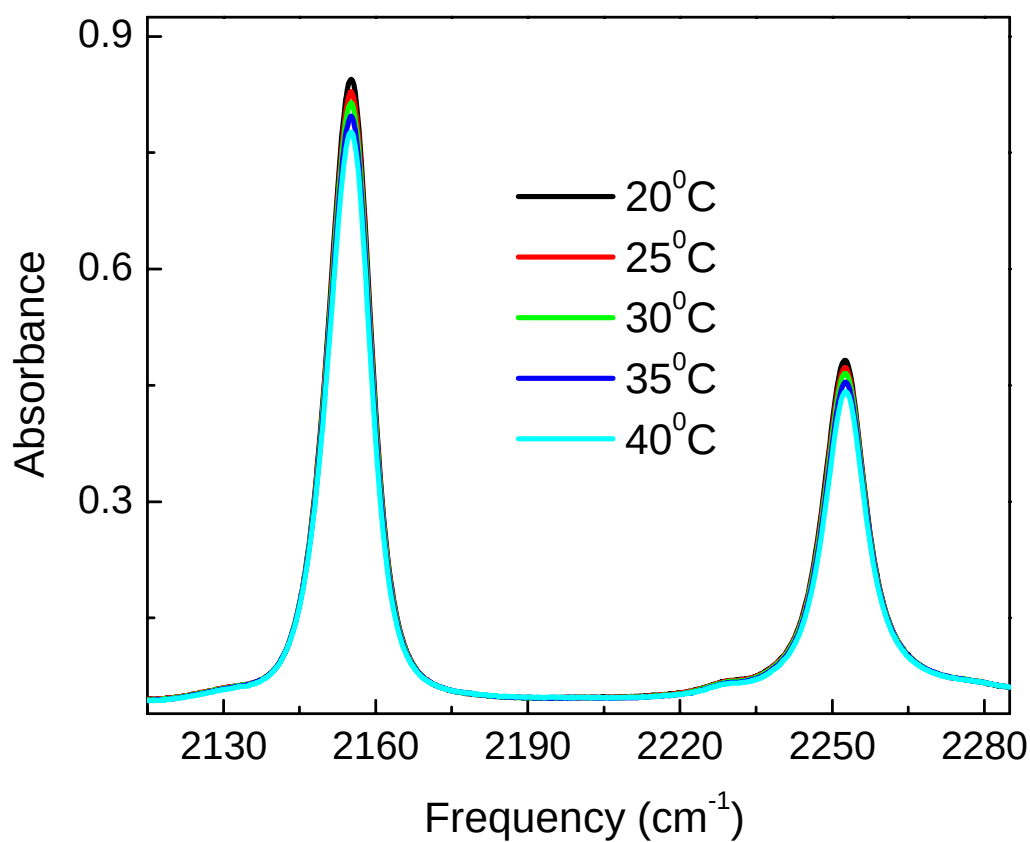


Figure S3. Temperature dependent FTIR spectra of $\text{C}_6\text{H}_5\text{SeCN}/\text{Cl}_3\text{CD}$ (1/1 molar ratio) mixed liquid. The absorption cross sections for both vibrational modes decrease with the increase of temperature. Both temperature increase and decrease procedures were performed to obtain reliable data.

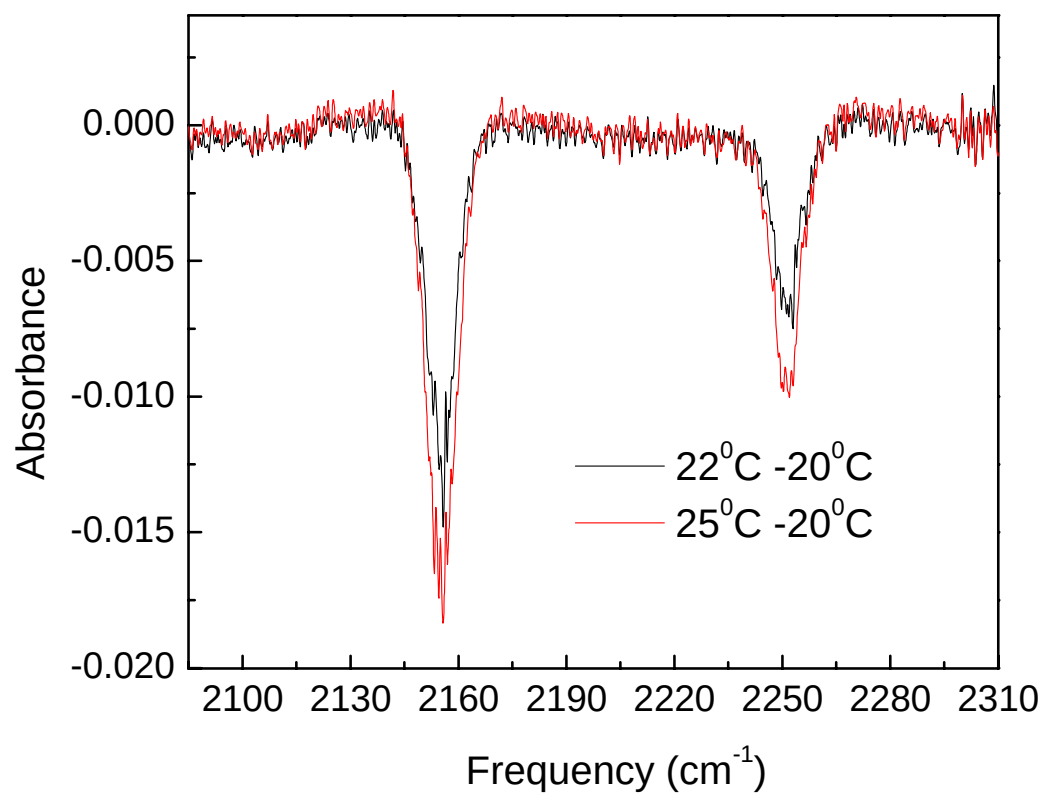


Figure S4. Temperature different FTIR spectra. Increasing temperature clearly produces bleachings.

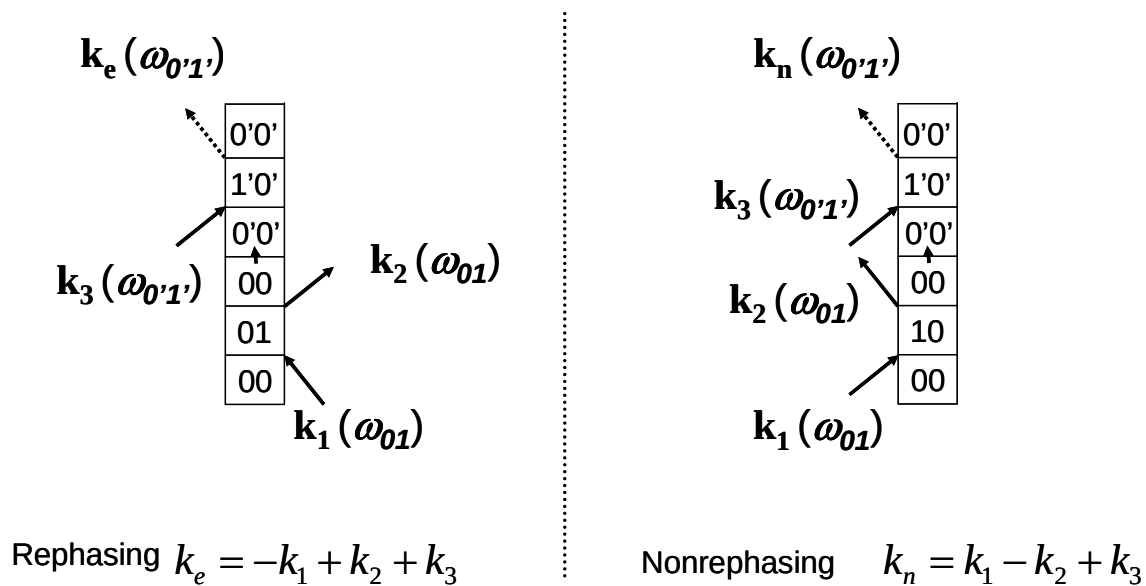


Figure S5. Feynmann diagrams showing how heat induced by vibrational relaxation of one mode creates absorption transparency on the other mode and therefore produces cross red peak (2155 cm^{-1} , 2252 cm^{-1}). The first interaction frequency (the x-coordinate in 2D IR spectra) ω_{01} is the CN 0-1 transition frequency 2155 cm^{-1} , and the emission frequency (the y-coordinate in 2D IR spectra) $\omega_{0'1'}$ is the CD 0-1 transition frequency 2252 cm^{-1} . During the population period after the 2nd interaction, heat from the CN excitation relaxation creates the CD ground state bleaching ($0'0'$). These two diagrams are also suitable for mode-specific vibrational energy transfers induced ground state bleedings. In such a scenario, during the population period, the energy transfer from one mode to the other, e.g. from the 1st excited of CD to that of CN, inevitably induces the ground state bleaching of CN since some of CN has accepted energy from CD and leave the ground state to its 1st excited state. Because theoretically heat or vibrational energy transfers induced ground state bleedings can be expressed with the same Feynman diagrams, experimentally the appearances of such red cross peaks can't be used as the evidence of mode-specific vibrational energy transfers.

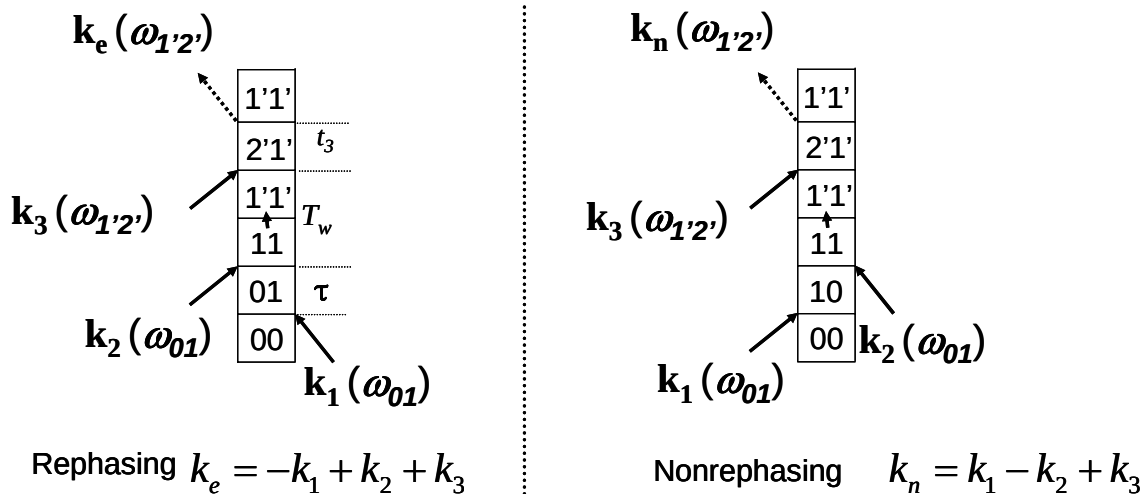
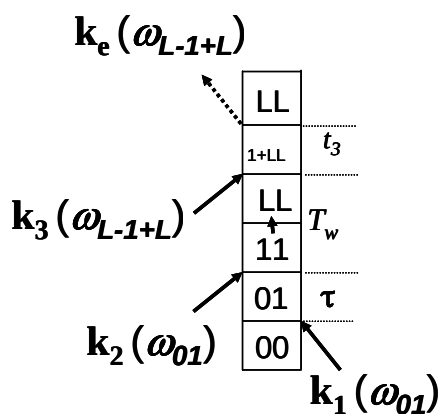
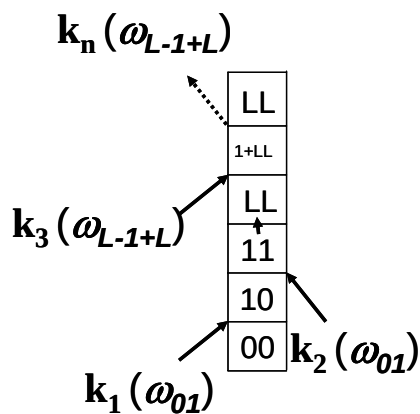


Figure S6. Feynman diagrams showing the origins of mode-specific energy transfer from CD to CN blue cross peak (2252 cm^{-1} , 2130 cm^{-1}). The first interaction frequency (the x-coordinate in 2D IR spectra) ω_{01} is the CD 0-1 transition frequency 2252 cm^{-1} , and the emission frequency (the y-coordinate in 2D IR spectra) $\omega_{1'2'}$ is the CN 1-2 transition frequency 2130 cm^{-1} . During the population period, the excitation of CD 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.



Rephasing $k_e = -k_1 + k_2 + k_3$



Nonrephasing $k_n = k_1 - k_2 + k_3$

Figure S7. Feynman diagrams showing the origins of vibrational relaxation induced blue peak (2252 cm^{-1} , 2241 cm^{-1}). The first interaction frequency (the x-coordinate in 2D IR spectra) ω_{01} is the CD 0-1 transition frequency 2252 cm^{-1} , and the emission frequency (the y-coordinate in 2D IR spectra) ω_{L-1+L} is the CD combination band transition frequency 2241 cm^{-1} . During the population period, the excitation of CD stretch (11) transfers to other mode(s) LL strongly coupled to it. The third interaction excites the CD 0-1 transition again while LL is (are) on the 1st excited state. The 0-1 transition frequencies are different, depending on whether LL is (are) on the ground state.

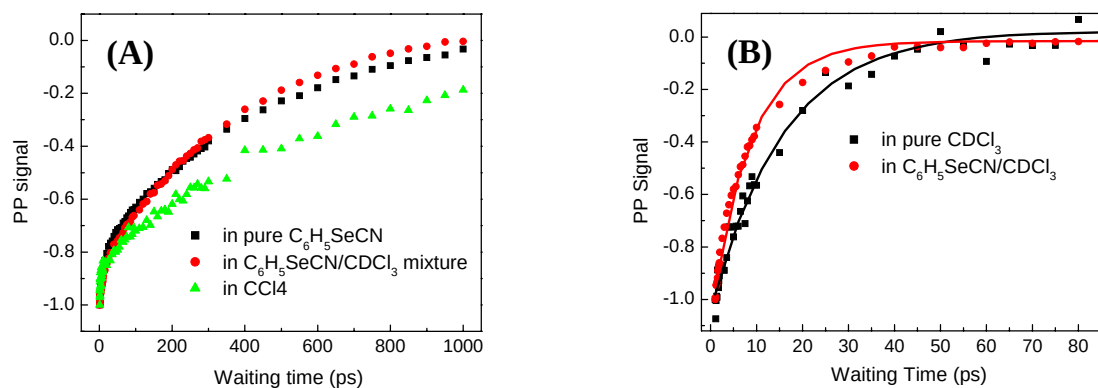


Figure S8. Vibrational lifetimes of CN and CD in different solvents. The effects of solvents on the vibrational lifetimes are apparent and are not easy to predict. For instances, the apparent vibrational lifetime of CD in the $C_6H_5SeCN/CDCl_3$ mixture is smaller than in pure $CDCl_3$ (B), while it is more complex for the CN (A): in the mixture, CD decays slower first and then faster than in its pure liquid.

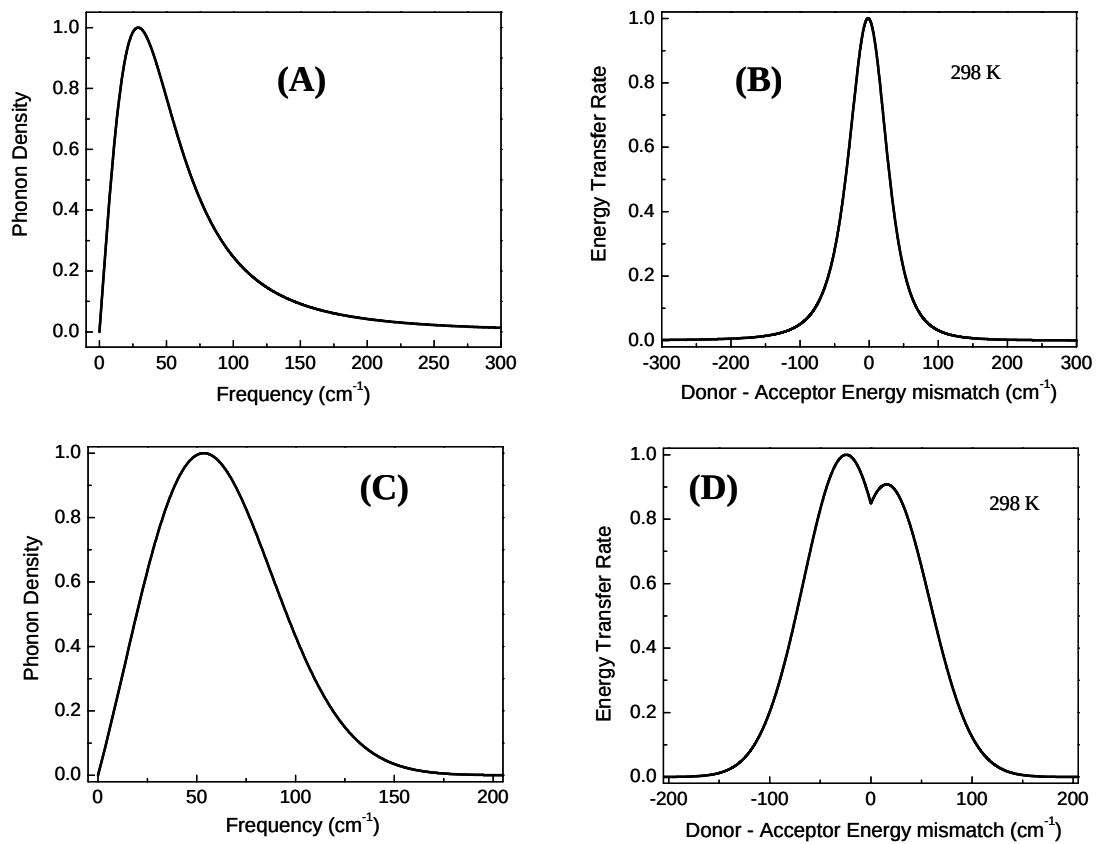


Figure S9. Densities of states and vibrational energy transfer rates calculated based on the densities of states and theory¹.

(A) Density of states calculated based on equation:

$$\rho(\omega) = \text{const.} \cdot \frac{\omega}{(B^2 - \omega^2)^2 + C^2 \omega^2}, \quad (\text{eq.1})$$

where $B = 50 \text{ cm}^{-1}$ and $C = 100 \text{ cm}^{-1}$;

(B) Energy transfer rate constant calculated based on (A) and equation:

$$k = n_{\omega}(1 + n_{\Omega+\omega})\rho_{\Omega+\omega}C_{\Omega+\omega} + (1 + n_{\omega})(\alpha + n_{|\Omega-\omega|})\rho_{|\Omega-\omega|}C_{|\Omega-\omega|}, \quad (\text{eq.2})$$

where $n_E = (e^{\frac{\hbar E}{kT}} - 1)^{-1}$, Ω is the frequency of donor, ω is the frequency of acceptor, ρ is the density of state, and C is the coupling constant assumed to be constant.

$\alpha = 1$, if $\Omega > \omega$; $\alpha = 0$, if $\Omega < \omega$. From the calculation, $\frac{k_{97\text{cm}^{-1}}}{k_{-97\text{cm}^{-1}}} = 0.62$ and $\frac{k_{-20\text{cm}^{-1}}}{k_{-97\text{cm}^{-1}}} = 14$;

(C) Density of states calculated based on equation:

$$\rho(\omega) = \text{const.} \cdot \omega \cdot e^{-\left[\frac{\omega - \omega_0}{\Delta\omega}\right]^2}, \quad (\text{eq.3})$$

where $\omega_0 = 20 \text{ cm}^{-1}$ and $\Delta\omega = 60 \text{ cm}^{-1}$;

(D) Energy transfer rate constant calculated based on (C) and eq.2. From the calculation,

$$\frac{k_{97 \text{ cm}^{-1}}}{k_{-97 \text{ cm}^{-1}}} = 0.62 \quad \text{and} \quad \frac{k_{-20 \text{ cm}^{-1}}}{k_{-97 \text{ cm}^{-1}}} = 4.3.$$

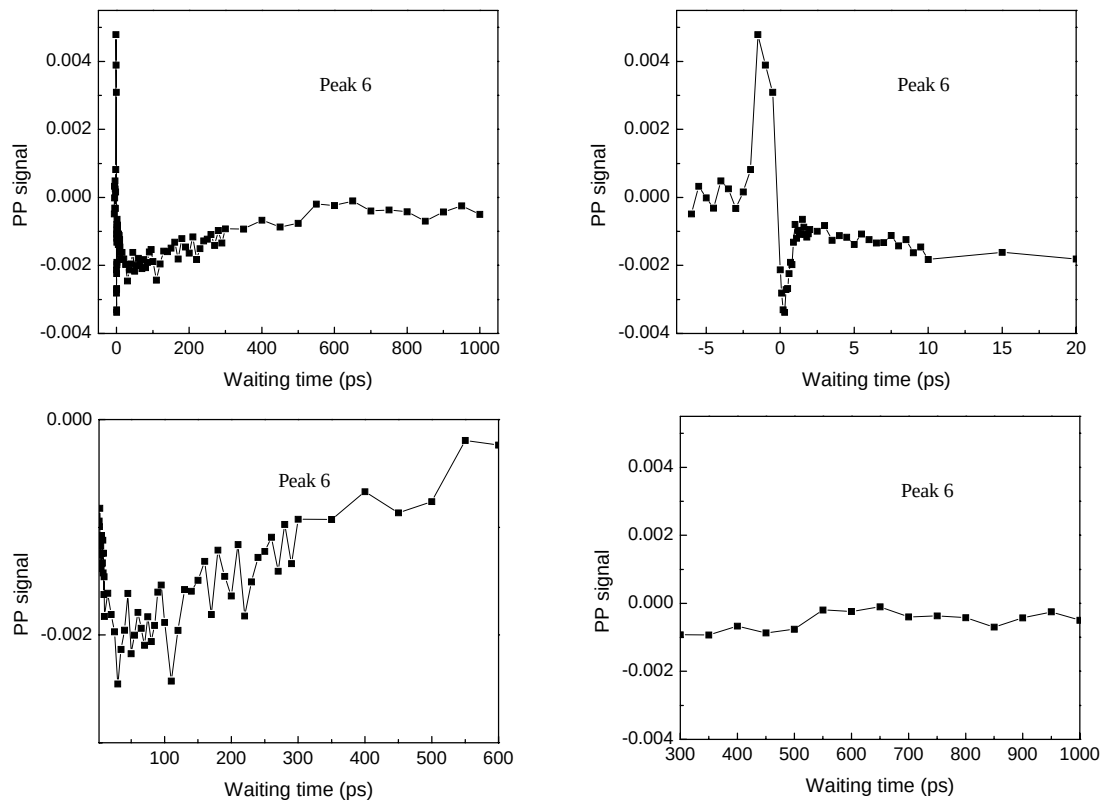


Figure S10. Pump/probe data of Peak 6 with negative waiting times

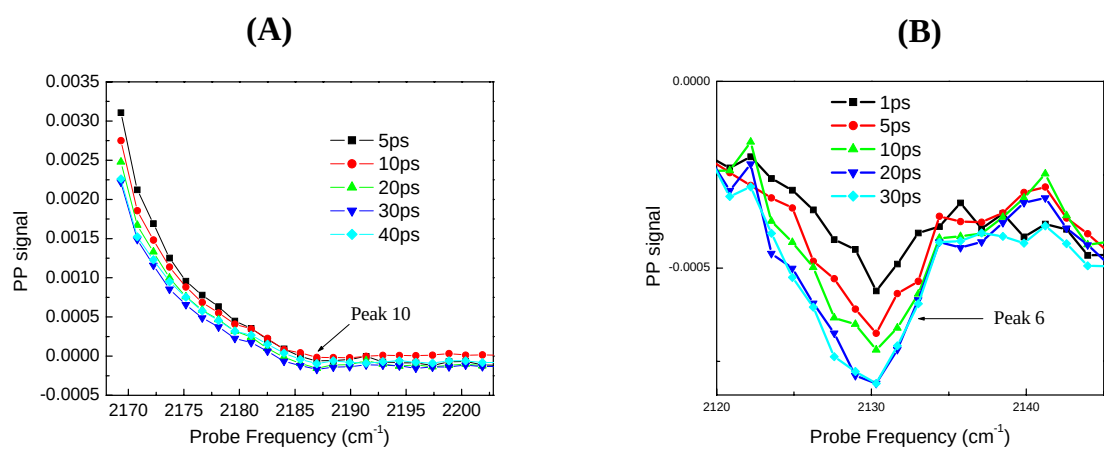


Figure S11. Intensities of Peak 10 and 6 in the frequency domain. Peak 10 can hardly be observed, probably caused by the cancellation of Peak 3. The growth of Peak 6 is clearly visible in (B).

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