A relaxation-assisted 2D IR spectroscopy method

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A method of two-dimensional infrared (2D IR) spectroscopy called relaxation-assisted 2D IR (RA 2DIR) is proposed that utilizes vibrational energy relaxation transport in molecules to enhance cross-peak amplitudes. This method substantially increases the range of distances accessible by 2D IR and is capable of identifying long-range connectivity patterns in molecules. RA 2DIR is illustrated in interactions among CN and CO modes in 3-cyanocoumarin and 4-acetylbenzonitrile, where the distances between the CN and CO groups are ~3.1 and ~6.5 Å, respectively. A 6-fold increase in cross-peak amplitude was observed in 4-acetylbenzonitrile when the dual-frequency RA 2DIR method was used.

two-dimensional infrared (2D IR) spectroscopy: relaxation-assisted 2D IR (RA 2DIR) method

Development of new methods for determining the 3D structures of molecules in solution is an important challenge in chemistry. Recently introduced in the pioneering works of Hochstrasser and colleagues (1, 2), two-dimensional infrared (2D IR) spectroscopy has demonstrated its strong potential for measuring molecular structures in solution under physiological conditions (2–10). 2D IR and 2D NMR correlation methods have many analogies (11). The cross-peaks in 2D IR spectra originate from pairwise interactions of vibrational modes (vs. nuclear spins for 2D NMR), offering a measure of the distances between interacting vibrational modes (vs. spins). Readily measurable anisotropy of the cross-peaks in 2D IR reveals another important type of structural information, the mutual orientation of the transition dipoles of interacting modes, vide infra (12). Although 2D IR methods have been successfully applied to the study of small molecules and peptides, the measurement of structural constraints in macromolecules such as proteins remains a challenge. Here, we propose a method that uses vibrational relaxation and vibrational energy transport in molecules to significantly enhance the cross-peaks measured with 2D IR for modes separated by distances >4–5 Å. This approach substantially increases the range of distances accessible by 2D IR and is capable of identifying vibrational modes separated by multiple bonds and of delivering the long-range bond connectivity patterns in a way similar to that of the total correlation spectroscopy method of 2D NMR (13) and its heteronuclear version, heteronuclear multiple bond correlation. Relaxation-assisted 2D IR (RA 2DIR) enhances the potential of weak modes in 2D IR and allows their convenient use as structural reporters.

In general, as structural labels, vibrational modes have the advantage of being very compact compared with, for example, FRET labels. However, the choice of vibrational labels for structural measurement in macromolecules by using 2D IR is not obvious. Thus far, most 2D IR cross-peak measurements have been performed by using strong IR stretching modes, such as C=C, O=O, O–H, N–H, and C–N. However, these modes are highly abundant in biopolymers, and isotope substitution is required in order to decouple the label from the rest of the modes. 13C18O isotopic substitution in the CO group shifts the CO stretching frequency at ~1,650 cm⁻¹ down by ~60–65 cm⁻¹, making it a promising vibrational label (14). However, the presence of very strong diagonal CO peaks reduces the dynamic range for the cross-peak measurements, diminishing the range of accessible intermode distances. O–H and N–H modes are less convenient as 2D IR labels because the isotope substitution of nitrogen or oxygen atoms generates only very small frequency shifts, whereas the protons in these groups are generally exchangeable (10). Labeling with groups not often present in organic molecules, such as N₂H, has not yet been sufficiently explored in 2D IR. Therefore, although there has been steady progress in 2D IR, including new experimental approaches (15–17), accessing structural constraints for molecules as large as proteins is still a challenge.

The use of weaker modes as 2D IR labels is promising, although it too is associated with experimental challenges. First, there is a much wider choice of weak modes and labels suitable for particular experimental conditions, including those in the water transparency regions. Second, by selecting mode pairs comprising modes of substantially different frequencies, the cross-peaks can be well separated from the strong diagonal peaks. Diagonal peaks can be largely reduced, or even completely eliminated, by using the dual-frequency 2D IR approach (8, 18). We have recently demonstrated the implementation of weak but localized C≡N stretching modes as structural labels in 2D IR (18). The cross-peaks originating from interactions of CN modes with C≡O and C≡C modes provided convenient structural handles (18). Furthermore, we have shown that extremely weak C–D modes in alkyl groups, having extinction coefficients of only ~1 M⁻¹cm⁻¹, form a useful structural reporter, and that interactions among CD and CN modes can be readily measured with dual-frequency 2D IR (8).

The difficulty in working with weak modes is associated with small cross-peaks, because the cross-peak amplitude is proportional to the square of the weak-mode transition moment. Although the cross-peak amplitude is typically strong enough when the modes are spatially close (18), it is expected to decay rapidly as a function of the mode separation distance (12). A small range of intermode distances accessible by 2D IR using weak IR modes can diminish the applicability of such structural labels. In this article, we describe an approach for measuring 2D IR spectra that allows one to substantially increase the range of distances accessible by 2D IR. This method utilizes vibrational relaxation and intramolecular vibrational energy redistribution (IVR) processes to enhance the cross-peak amplitudes in 2D IR spectra.

Because IVR is the core process that determines the enhancement of the cross-peaks in RA 2DIR, we discuss it briefly here. Vibrational relaxation, energy transfer between specific modes (6,
The linear IR spectrum of 3-cyanocoumarin (Fig. 1) is shown in Fig. 2. The relaxation rates are determined by several factors, including the local density of states, the amplitude and rate of frequency fluctuations, and the intermediate coupling matrix elements (22, 23, 26). The complexity of IVR and vibrational energy transport processes originates from the nature of vibrational modes, which are often delocalized in molecules but to a different extent (22, 23, 27). This mode delocalization facilitates mode overlap and increases the rate of the IVR process. On the other hand, the mostly localized character of some modes is a source of fractal effects in transport in molecules on the length scales from angstroms to tens of angstroms is complex and less well understood than heat transport processes in molecules on angstrom scales. An RA 2DIR method is used to follow vibrational energy flow in molecules on angstrom scales (28). Although the main advantage of using the RA 2DIR approach lies in its capacity as a structural method, it also provides a convenient means for studying energy transport processes in molecules on angstrom scales. An RA 2DIR method is proposed here and is tested on CN and CO mode interactions in 3-cyanocoumarin and 4-acetylbenzonitrile (AcPhCN).

**Results and Discussion**

The linear IR spectrum of 3-cyanocoumarin (Fig. 1) is shown in Fig. 2. Three vibrational modes are of importance for this work: C=\(\equiv\)N (2,240 cm\(^{-1}\)), C=O (1,744 cm\(^{-1}\)), and C=C (1,613.7 cm\(^{-1}\)); the latter bond is located at the third and fourth coumarin-ring carbon atoms (Fig. 1). For both samples, 3-cyanocoumarin and AcPhCN, the optical density at the CO peaks was 0.3–0.4. For the cross-peak measurements, the pulse spectra were tuned so that the \(k_1\) and \(k_2\) beams overlapped with the CN peak and the \(k_3\) and local oscillator (LO) beams overlapped with the CO peak (Fig. 2).

**Qualitative Analysis of the 2D IR Spectrum at \(T = 670\) fs.** The dual-frequency absorptive spectrum of 3-cyanocoumarin obtained at time delay \(T\) (T-delay) of 670 fs is shown in Fig. 3 and 4. The spectra of the mid-IR pulses used for this experiment are shown in Fig. 2. Three pairs of peaks are prominent. The pair at approximately (1,743, 2,239), originating from the interaction of the CN and CO modes, dominates the spectrum. Surprisingly, the diagonal CO-mode peaks can also be seen at approximately (1,743, 1,743 cm\(^{-1}\)). The diagonal peaks are observed because the \(k_1\) and \(k_2\) pulses, centered at 2,239 cm\(^{-1}\), have nonzero intensity at 1,743 cm\(^{-1}\) that only amounts to 2 \times 10^{-3} of the intensity of 2,239 cm\(^{-1}\) maximum. The amplitude of the diagonal peaks increases \(\approx 500\) times when the \(k_1\) and \(k_2\) spectra are centered at 1,743 cm\(^{-1}\).

In addition, another cross-peak pair, which is derived from interaction of the CN and CC modes, is seen in the 2D spectrum at approximately (1,605, 2,239 cm\(^{-1}\)) (Fig. 3). The amplitude of this peak is only \(\approx 2\) times smaller than that of the CO/CN cross-peaks, whereas the intensity of the \(k_3\) and LO pulses at \(\omega_{CC}\) is \(> 5\) times smaller than that at \(\omega_{CC}\), indicating that interaction among the CC and CN modes is substantially stronger than interaction among the CO and CN modes.

Several characteristics of the 2D IR spectra can be used to determine the off-diagonal anharmonicity values. One is the amplitude of the cross-peaks relative to the amplitude of the diagonal peaks. By using the measured light intensities of all pulses at the wavelengths involved, as well as the known value of diagonal anharmonicity of the CO mode, the CN/CO off-diagonal anharmonicity can be obtained by global modeling.

Alternatively, the exact frequencies of the peaks in 2D IR spectra can provide an estimate of the off-diagonal anharmonicities. Note that the peak separation in a peak pair reveals the respective anharmonicity only if the anharmonicity is larger than the width of the transition at \(\omega_0\). When the off-diagonal anharmonicity is small compared with the linewidths, the peak separation in the peak pair is determined solely by the width of the transition (19). However, the relative positions (\(\omega_0\)) of the diagonal and cross-peaks can be used to determine the anharmonicities. Specifically, the \(\omega_0\) frequency of the crossing-point on the zero contour and the line connecting the minimum and maximum in the peak pair, denoted as \(\omega_0\), is very informative (Fig. 3). The diagonal CO peaks are formed by the negative peak at \(\omega_{CO} - \Delta CO\) and the positive peak at \(\omega_{CO} + \Delta CO\), where \(\omega_{CO}\) and \(\Delta CO\) are the 0\(\rightarrow\)1 transition frequency and the diagonal anharmonicity of the CO mode, respectively (Fig. 4 B and C). If the difference in width and amplitude for the positive and negative peaks of a peak pair are neglected (weak anharmonicity limit), the \(\omega_0\) frequency is located in the middle, between the two peaks. Therefore, for the diagonal CO peak, the \(\omega_0\) frequency equals \(\omega_{CO} - \frac{1}{2}\Delta CO\). The CO/CN cross-peaks are also formed by two peaks: the negative peak at \(\omega_{CO} - \Delta CNCO\) and the positive peak at \(\omega_{CO} + \Delta CNCO\), where \(\omega_{CN}\) is the 0\(\rightarrow\)1 transition frequency of the CN mode and \(\Delta CNCO\) is the off-diagonal anharmonicity for the CN/CO interaction. The \(\omega_0\) frequency of the CN/CO cross-peak is also in the middle, between the \(\omega_{CO} + \Delta CNCO\) and \(\omega_{CO} - \Delta CNCO\) frequencies, namely at \(\omega_{CO} - \frac{1}{2}\Delta CNCO\). Therefore, the shift between the \(\omega_0\) frequencies for the diagonal and the cross-peaks is expected to be \(\omega_0^{cross}(\omega_{CO}) - \frac{1}{2}(\Delta CO - \Delta CNCO)\). The experimental value of the shift of 6.5 \pm 0.5 cm\(^{-1}\) measured in the \(T = 670\) fs spectrum (Fig. 3) provides an estimate of the off-diagonal anharmonicity at 2 \pm 1 cm\(^{-1}\).

**Two-Dimensional IR Spectra Measured at Various T-Delay Times: Qualitative Analysis.** To investigate how vibrational relaxation dynamics affect the spectra, we measured the 2D IR spectra at several T-delays, two of which, \(T = 2\) and 4 ps, are shown in Fig. 3.
expected, these spectra exhibit peaks similar to those seen in the spectrum obtained at $T = 670$ fs, but surprisingly the amplitudes of these peaks are almost as large as those in the $T = 670$ fs spectrum. Indeed, the lifetime of the excited CN mode has been measured at 1.4 ± 0.2 ps by a pump-probe method. The CN excited-state population at a T-delay of 4 ps drops by 10 times smaller than that in the $T = 670$ fs spectrum. Because such decrease was not observed experimentally, we concluded that vibrational relaxation and IVR processes, which have little influence on the spectra with small $T$ values, are strongly affecting those measured at large T-delays.

In addition to weakly decreasing the CO/CN cross-peak amplitude in the spectra at 0.67, 2, and 4 ps $T$-delay, the $\omega_2$ frequency of the CO/CN cross-peak changes with the T-delay. The following qualitative analysis of the spectra at various T-delays is based on comparison of the $\omega_2$ frequencies for the CO-diagonal ($\omega_2$(CO)) and CN/CO-cross ($\omega_2$(cross)) peaks. The shift value [$\omega_2$(cross) $-$ $\omega_2$(CO)] changes from 6.5 ± 1 cm$^{-1}$ in the $T = 670$ fs spectrum to 6 ± 1 cm$^{-1}$ and 1.2 ± 0.5 cm$^{-1}$ in the spectra at 2 and 4 ps, respectively. At 4 ps, the major part of the excited CN mode population has been relaxed by the IVR process to other modes, mainly those in the same molecule. Vibrational relaxation can populate the modes, denoted as X, that are strongly coupled to the CO mode and that therefore have large CO/X anharmonicities, $\Delta_{XCO}$ (Fig. 4A). We concluded that the cross-peaks at large T-delays derive from interactions of such modes, X, with the CO mode. Typical Feynman diagrams responsible for such cross-peaks are shown in Fig. 4C and D. The experimentally observed drastic shift of $\omega_2$ to smaller frequencies indicates that IVR populates the modes, X, that have $\Delta_{XCO}$ anharmonicities larger than the direct-coupling CN/CO anharmonicity, $\Delta_{CO,CN}$. Note that the amplitude of the cross-peaks remains nearly unchanged until $T \geq 6$ ps, whereas the peak character changes from the direct-coupling (Fig. 4B) to the relaxation-induced cross-peaks (Fig. 4C and D).

Vibrational relaxation from the CN mode can also lead to population of the CO mode (X=CO); however, modeling showed that such a relaxation pathway is not the dominant pathway. The X state comprises a variety of yet-unidentified modes interacting with the CO mode, and the off-diagonal anharmonicity $\Delta_{XCO}$ represents an averaged anharmonicity over multiple states populated by IVR. However, because the amplitude of the cross-peaks featuring small anharmonicities is proportional to the anharmonicity value, strong interactions with large anharmonicities dominate the cross-peak.

To clarify various contributions to the cross-peaks at longer T-delays, the rephasing ($\omega_2$, $T$) 2D spectra were measured. The $\omega_2$ spectra acquired in this way include contributions from all peaks with the same $\omega_2$ that appeared in the 2D spectrum measured under the same experimental conditions. In other words, the $\omega_2$ spectrum is a sort of projection of the 2D spectrum onto the $\omega_2$ axis. Therefore, the CO peak in the $\omega_2$ spectra, although dominated by CN/CO cross-peaks, also contains contributions from the CO-diagonal peaks. A shift to smaller frequencies at larger $T$ values was observed for both the CO and CC peaks [see supporting information (SI) Fig. 10]. The peak amplitude and peak frequency are plotted for both peaks as a function of $T$-delay (Fig. 5). An interference of the cross-peak and diagonal-peak contributions, seen as an oscillatory pattern, was introduced by small changes in $T$ values for the scans at different T-delays.

Interestingly, the two dependencies (i.e., the peak amplitude and the peak frequency) have very different time behaviors. The amplitudes of both the CO and CC peaks decay with the characteristic time of $\approx$14 ps, which is much longer than the CN excited-state lifetime ($T_{1/2}$ = 1.4 ps). The peak frequencies of both peaks shift to smaller values by $\approx$3–4 ps. The shift is $\approx$7 cm$^{-1}$ for the CO peak and $\approx$4 cm$^{-1}$ for the CC peak. Note that the peak frequency of the absolute-value spectrum is approximately equal to the $\omega_2$ frequency of the peak pairs. The shift occurs when the relaxation-induced peaks overcome the direct-coupling cross-peaks.

Fig. 3. Two-dimensional IR absorptive spectra of cyanocoumarin measured at T-delays of 670 fs (A), 2 ps (B), and 4 ps (C). The zero-contour $\omega_2$ frequencies are shown. In B Inset, the amplitude of the upper-left part of the spectrum was multiplied by a factor of 3.

Fig. 4. Energy diagram (A) and rephasing Liouville pathways describing the direct-coupling (B and C) and relaxation-assisted (C and D) cross-peaks.
peaks. Therefore, at T-delays >3–4 ps, the contributions from the excited states populated by IRV dominate the cross-peaks; even at 5 ps, the amplitude of the cross-peaks is very strong.

Spectral Modeling and Relaxation Scheme
The heterodyned time-domain third-order signal giving rise to cross-peaks at \(\omega_1, \omega_2\) in the Bloch approximation is given by

\[
S_{RNR}(\tau, T, t) = (zzzz)\mu^2 e^{i (\omega_1 t - \omega_2 t)} \frac{1}{2} e^{-\frac{\gamma_1 \tau - \gamma_2 \tau}{T_1} - \frac{\sigma_1^2}{2} - \frac{\sigma_2^2}{2} - T_2^2} e^{i \omega_1 \tau + \omega_2 \tau},
\]

where the upper and lower signs correspond to the rephasing and nonrephasing experiments, respectively; \((zzzz) = 1 + \frac{\gamma_0 (3 \cos^2 \theta - 1) e^{-\tau/\tau_0}}{2}\) is the rotation relaxation factor for z polarization for all four pulses (29); \(\tau_0\) is the mean rotation time; \(\Delta\) is the off-diagonal anharmonicity; \(T_2^2\) is the population relaxation time of the \(\omega_1\) mode; and \(\gamma_1, \sigma_1, \sigma_2,\) \(\mu_1,\) and \(\mu_2\) are the total dephasing time, inhomogeneous width, and transition dipole of the fundamental transitions with \(\omega_1\) and \(\omega_2\) frequencies, respectively. The distributions of \(\omega_1\) and \(\omega_2\) frequencies were assumed to be static, with the correlation coefficient \(f\) given by \(\langle \delta \omega_1, \delta \omega_2 \rangle / \sigma_{\omega_1} \sigma_{\omega_2}\), where \(\delta \omega_1, \delta \omega_2\) are the frequency deviations from the respective mean frequencies. The diagonal signals were also modeled with Eq. 1, taking \(\mu_2 = \sqrt{2} \mu_1, f = 1\) (9, 30), \(\omega_1 = \omega_0\), and \(\Delta = \Delta_1\), where \(\Delta_1\) is the value of the diagonal anharmonicity. Note that the CN/CO cross-peaks measured with zzzz polarizations are not very sensitive to rotational motion in both 3-cyanoocumarin and AcPhCN. This is because the angle between the transition moments of the CN and CO modes in both compounds is \(\approx 60^\circ\), which is close to the magic angle. Therefore, the amplitude of the cross-peak is expected to change, as a result of rotational relaxation, by only \(\approx 10\%\). Also, orientational motion during \(\tau\) and \(t\) time intervals does not significantly influence the signals because the mean rotation time in methylene chloride was estimated to be >6 ps for both compounds (31), which is much larger than the \(\tau\) and \(t\) scanning ranges.

A minimal relaxation scheme sufficient to describe all spectral features includes four modes: CN, CO, CC, and X. For every pair of modes, A and B, the rate constant of the A-to-B reaction (\(k_{AB}\)) was connected with the B-to-A reaction rate constant (\(k_{BA}\)) through the Boltzmann factor, \(k_{AB}/k_{BA} = \exp[\hbar(\omega_\lambda - \omega_\beta)/(kT)]\). The pairwise interactions among the four modes were explicitly included. The values of the lifetimes for the CN, CO, and CC modes were allowed to change within the error bars to their experimentally measured values of 1.4, 1.3, and 2.2 ps, respectively. Six experimental dependencies (i.e., the four shown in Fig. 5 plus the linear spectrum and the CN population delay) were fitted globally. The parameters obtained (see Fig. 5 legend) were used to generate the fitting curves (Fig. 5). The fit required having a state that remains excited for >25 ps and is strongly coupled to the CO mode. The lifetime of the X state (\(\approx 27\) ps) can be understood as the cooling time of the molecule. The cooling time is known to depend on the amount of vibrational excess energy and may aid in the identification of the energy range for the X mode (20).

CN/CO Cross-Peaks for AcPhCN. Dual-frequency 2D IR measurements were performed on the CN and CO modes in AcPhCN. As expected, the direct-coupling CN/CO cross-peaks for modes separated by \(\approx 6.5\) Å appeared to be very weak and noisy. However, with an increase in the T-delay, \(T\), the cross-peak amplitude increases >6-fold because of the appearance of the relaxation-assisted cross-peaks (Fig. 6). Large enhancement for relaxation-assisted cross-peaks is observed as a result of the large distance between the modes; the direct coupling at such distances is small, but vibrational excitation transferred from the excited CN modes can reach the CO site efficiently. The cross-peak amplitude reaches...
Because the energy transport model used is oversimplified, the vibrational excitation is preserved in the molecule for stronger than the through-space electric coupling with solvent magnitude slower because the mechanical through-bond coupling transport dominantly proceed along covalent bonds in a molecule. It is known that vibrational energy equilibration and are responsible for propagation of the excess energy along the steps must occur during a 10-ps time window. These relaxation steps of vibrational modes.

Fig. 8. Schematic representation of fundamental vibrational states as a function of their location in a molecule. Horizontal bars show spatial extent of vibrational modes.
It is interesting to speculate how strong enhancement of the cross-peak amplitude can be achieved. Clearly it depends on the type of modes used, the initial distance between the modes, and the size and structure of the molecule. In the limiting case that the energy transport along the molecule can be treated as pseudo-1D, the maximal temperature reached at distance \( k \) from the initial heating spot depends on distance as \( R^{-1} \). Although such a weak distance-dependence is encouraging, the actual RA 2DIR cross-peak amplitude depends on the frequencies of the modes \( \omega_0, \omega \) coupled with the \( \omega_0 \) mode (CO in this work). On the other hand, the distance-dependence for the direct-coupling peaks depends on the coupling mechanism. For the electric coupling of the molecules in which heat transport can be treated as pseudo-1D, diffusion, a simple estimation can be performed. For linear time dependence for the direct-coupling peaks depends on the coupling mechanism. For the mechanical coupling is the dominant coupling mechanism. Estimations show that \( >20 \) fold enhancements of the cross-peak amplitudes might be possible using the RA 2DIR approach.

Conclusions

Interestingly, the cross-peaks caused by vibrational relaxation in 2D IR spectra have been observed before \( (6, 7, 19, 20) \), but their capabilities for structural measurement have not been foreseen. We analyzed the relaxation phenomena and found that, under certain experimental design conditions, it can lead to a very strong enhancement of cross-peak amplitudes. Here we have proposed an RA 2DIR structural method and have demonstrated that it can provide a useful handle in measuring weak mode-to-mode interactions in molecules and can deliver cross-peaks that are much stronger than direct-coupling cross-peaks. This enhancement will allow observation of cross-peaks for modes separated by large distances. It is conceivable that \( >3 \) times larger distances will be accessible with RA 2DIR than with traditional 2D IR. Two types of structural constraints can be measured by using RA 2DIR cross-peaks. First, the angles between transition moments of the modes accessed by IR pulses can be determined by anisotropy measurements, in the same way as for the direct-coupling peaks. Second, the T-delay dependence of the cross-peak amplitude (Fig. 6) could be related to the distance between the groups by using theoretical modeling. We also suggest that the most probable candidates for the modes accepting vibrational energy and strongly coupled to the CO mode are those located on the same atoms as CO, specifically, the acetyl in-plane and out-of-plane bending and rocking modes. The RA 2DIR method can be implemented in various experimental settings, including the 2D IR pump-probe setup.

Experimental Methods

Dual-Frequency Heterodyned 2D IR Spectra.

The geometry of pulses used for the dual-frequency 2D IR experiments, and the notations used for the delays between the pulses, are shown in Fig. 9. The technical details of the pulse generation are given in SI Experimental Methods. The third-order signal emitted by the sample was picked at the phase-matching direction \( (-k_1 + k_2 + k_3) \) and mixed on a detector with the LO. The 2D \( (t, \tau) \) spectra were recorded and double Fourier-transformed to obtain \( (\omega, \omega_0) \) spectra. The rephasing spectra were collected, with the \( k_1 \) pulse arriving first and the \( k_2 \) pulse arriving second; for the nonrephasing spectra, the order of the first two pulses was reversed. The polarization direction was the same for all four beams. Absorptive 2D spectra were constructed as a sum of the real parts of the rephasing and nonrephasing spectra.

The \( (t, \tau) \) spectra were obtained by a Fourier transformation of the \( (t, T) \) 2D array along the \( T \) direction. The \( \tau \) delay in the measurements of the \( (t, T) \) array was varied in relation to the T-delay, according to the equation, \( \tau = 10 + 0.024 \times T \) fs. The modeling of these spectra was performed by using the same conditions.

Sample Preparation.

The samples were 89 mM 3-cyanocoumarin and 125 mM AcPhCN in dichloromethane, held in a 50-\( \mu \)m optical path length cell with CaF\(_2\) windows.

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