Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Thermal Lensing Effect of CS_2 Studied with Femtosecond Laser Pulses

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This **Supporting Information** includes two sections: A and B. In Section A, titled "Derivation of the electromagnetic wave equation", we amply derive the frequency-domain electromagnetic wave equation for an individual pulse in an 18 fs-pulse train, say the ith one, driven by the third-order nonlinear polarization corresponding to librational excitation via SRS. In Section B, titled "Simulation of the OKE signals", we simulate the signals of the optical heterodyned-detected OKE (OHD-OKE) corresponding to our experimental conditions.

A. Derivation of the electromagnetic wave equation

In the derivation of the electromagnetic wave equation, we consider the following four conditions of the pulse or the sample. Firstly, the electric field strength $\vec{E}'^{(\mathrm{i})}(z,r,\omega)$ is a quasi-plane wave disturbance with $\nabla\cdot\vec{E}'^{(\mathrm{i})}(z,r,\omega)$ nearly equal to 0. Secondly, the slowly varying amplitude of $\vec{E}'^{(\mathrm{i})}(z,r,\omega)$ (i.e., $\vec{E}''^{(\mathrm{i})}(z,r,\omega)$) varies with z much more slowly than e^{-ikz}. Thirdly, the sample satisfies the thin sample condition with its thickness 0.1 cm less than the diffraction length of the ω_c component of the pulse in it ($n\times z_0(\omega_c)$=0.12 cm with n=1.63 being CS_2's refractive index and $z_0(\omega_c)=7.5\times10^{-2}$ cm being the diffraction length in free space). Finally, the sample is in full thermodynamic equilibrium before immediately interaction with the pulse.

When the sample position z ranges between z_f and z_f+L with z_f denoting its front surface position relative to the beam waist, the frequency-domain third-order nonlinear polarization induced by the ith pulse can be written as

$$\vec{P}'^{(3,\mathrm{i})}(z,r,\omega)=\varepsilon_0\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi^{(3)}(\omega;\omega',\omega_a,\omega_b)\vdots\vec{E}'^{(\mathrm{i})}(z,r,\omega')\cdot\vec{E}'^{(\mathrm{i})}(z,r,\omega_a)\cdot\vec{E}'^{(\mathrm{i})}(z,r,\omega_b)\,d\omega_b d\omega_a \tag{S1}$$

with $\omega'=\omega-\omega_a-\omega_b$. This polarization conversely drives the electromagnetic wave

$$\nabla\left[\nabla\cdot\vec{E}'^{(\mathrm{i})}\left(z,r,\omega\right)\right]-\nabla^2\vec{E}'^{(\mathrm{i})}\left(z,r,\omega\right)-\frac{\omega^2}{c^2}\vec{E}'^{(\mathrm{i})}\left(z,r,\omega\right)=\mu\omega^2\vec{P}'^{(3,\mathrm{i})}\left(z,r,\omega\right) \qquad \text{(S2)}$$

where μ represents the magnetic permeability of the sample (CS_2), nearly equal to that of the vacuum (μ_0) since the sample is nonmagnetic.

Since $\vec{E}'^{(\mathrm{i})}$ is a quasi-plane wave disturbance, divergence of it nearly equals zero. As a result, we can neglect the first term on the left hand side of eq.(S2). In addition, because the sample satisfies the thin sample condition with its thickness 0.1 cm less than the diffraction length of the ω_c component of the pulse in it $n\times z_0(\omega_c)$=0.12 cm (n=1.63 being CS_2's refractive index and $z_0(\omega_c)$= 7.5×10^{-2} cm being the diffraction length in free space), beam broadening or narrowing due to diffraction is negligible in the sample. Accordingly, we can neglect $\partial(r\partial\vec{E}'^{(\mathrm{i})}/\partial r)/(r\partial r)$ but retain $\partial^2\vec{E}'^{(\mathrm{i})}/\partial z^2$ in the expansion of $\nabla^2\vec{E}'^{(\mathrm{i})}$ in eq.(S2). This leads to

$$\frac{\partial^2\vec{E}'^{(\mathrm{i})}\left(z,r,\omega\right)}{\partial z^2}+\frac{\omega^2}{c^2}\vec{E}'^{(\mathrm{i})}\left(z,r,\omega\right)=-\mu\omega^2\vec{P}'^{(3,\mathrm{i})}\left(z,r,\omega\right). \qquad \text{(S3)}$$

Using the relations (see the description between eqs.(5) and (6) in the **Main Text**)

$$\vec{E}'^{(\mathrm{i})}\left(z,r,\omega\right)=\vec{E}''^{(\mathrm{i})}\left(z,r,\omega\right)\times e^{-i\left(kz+\omega T_{\mathrm{i}}\right)} \qquad \text{(S4)}$$

and

$$\vec{P}'^{(3,\mathrm{i})}\left(z,r,\omega\right)=\vec{P}''^{(3,\mathrm{i})}\left(z,r,\omega\right)\times e^{-i\left(kz+\omega T_{\mathrm{i}}\right)} \qquad \text{(S5)}$$

with $\vec{E}''^{(i)}(z,r,\omega)$ and $\vec{P}''^{(3,i)}(z,r,\omega)$ being the slowly varying amplitudes of $\vec{E}'^{(i)}(z,r,\omega)$ and $\vec{P}'^{(3,i)}(z,r,\omega)$ respectively, we can simplify eq.(S3) as

$$2ik\frac{\partial\vec{E}''^{(i)}(z,r,\omega)}{\partial z}=\mu\omega^2\vec{P}''^{(3,i)}(z,r,\omega). \quad \text{(S6)}$$

Since $\vec{E}''^{(i)}(z,r,\omega)$ changes with z much more slowly than e^{-ikz}, we have ignored the term $-\partial^2\vec{E}''^{(i)}(z,r,\omega)/\partial z^2$ on the left hand side.

When two monochromatic electric field strengths at angular frequencies ω_1 and ω_2 ($\vec{E}_{1(2)}(z,r,t)=\vec{E}_{10(20)}(z,r)\times(e^{i\omega_{1(2)}t}+e^{-i\omega_{1(2)}t})/2$) are used to excite a molecular motion via a specific SLS process in the sample (CS_2), two monochromatic third-order nonlinear polarizations at the same frequencies (one at ω_1 and the other at ω_2), $\vec{P}^{(3)}_{1(2)}(z,r,t)=\vec{P}^{(3)}_{10(20)}(z,r)\times(e^{i\omega_{1(2)}t}+e^{-i\omega_{1(2)}t})/2$, are induced. Their amplitudes are related to that of the electric field strengths as (ref.[24] of the **Main Text**)

$$\vec{P}^{(3)}_{10}(z,r)=\varepsilon_0\chi^{(3)}(\omega_1;\omega_1,\omega_2,-\omega_2)\vdots\vec{E}_{10}(z,r)\cdot\left|\vec{E}_{20}(z,r)\right|^2 \quad \text{(S7)}$$

and

$$\vec{P}^{(3)}_{20}(z,r)=\varepsilon_0\chi^{(3)}(\omega_2;\omega_2,\omega_1,-\omega_1)\vdots\vec{E}_{20}(z,r)\cdot\left|\vec{E}_{10}(z,r)\right|^2. \quad \text{(S8)}$$

Here $\chi^{(3)}(\omega_1;\omega_1,\omega_2,-\omega_2)$ depends on $(\omega_1-\omega_2\mp\Omega_m)$ in the same way that $\chi^{(3)}(\omega_2;\omega_2,\omega_1,-\omega_1)$ depends on $(\omega_2-\omega_1\pm\Omega_m)$ (ref.[29] of the **Main Text**). The "–" or "+" sign is adopted in the term $(\omega_1-\omega_2\mp\Omega_m)$ when $(\omega_1-\omega_2)$ is larger or smaller than 0. In connection with this condition, the "+" or "–" sign is used in

the term $(\omega_2-\omega_1\pm\Omega_m)$. Accordingly, $\chi^{(3)}(\omega_1;\omega_1,\omega_2,-\omega_2)$ equals $\chi^{(3)*}(\omega_2;\omega_2,\omega_1,-\omega_1)$ since they are both Hermitian. Moreover, they are nonzero only when $|\omega_1-\omega_2|$ falls within the range [$\Omega_m-\Delta\Omega_m/2$, $\Omega_m+\Delta\Omega_m/2$]. Note that $\vec{E}_{10}(z,r)$ and $\vec{E}_{20}(z,r)$ are of the same dimension as $\vec{E}_0^{(i)}(z,r,t)$ and $\vec{E}_0'^{(i)}(z,r,\omega)$ divided by time.

When an 18 fs-laser pulse with a spectrum width $\Delta\omega$ larger or comparable with Ω_m (m=l, d or p) is used to excite the inter-molecular motions via SLS, the corresponding third-order nonlinear polarizations cover the entire or part of the continuous spectrum of $\vec{E}''^{(i)}(z,r,\omega)$. However, with $\Delta\omega$ smaller than Ω_v, an 18 fs-laser pulse can hardly induce the intra-molecular vibration via SRS, the resultant third-order nonlinear polarization is then zero. In the following, we only deal with librational excitation by SRS, but the approach we take is suitable for excitations of the other two inter-molecular motions (diffusive reorientation and polarizability distortion) by SLS and intra-molecular vibration by SRS. In analogy to the requirements of $\omega_a=-\omega_b=\omega_1$ with $\omega=\omega_2$ and $\omega_a=-\omega_b=\omega_2$ with $\omega=\omega_1$ for $\chi^{(3)}(\omega;\omega,\omega_a,\omega_b)$ employed in eqs.(S7) and (S8), we substitute $\tilde{\chi}^{(3)}(\omega;\omega,\omega_a,-\omega_a)\times\delta(\omega_b+\omega_a)$ into eq.(S1) for $\chi^{(3)}(\omega;\omega,\omega_a,\omega_b)$ to derive the ith 18 fs pulse-induced third-order nonlinear polarization

$$\vec{P}''^{(3,i)}(z,r,\omega)=2\varepsilon_0\times\int_0^\infty\tilde{\chi}^{(3)}(\omega;\omega,\omega_a,-\omega_a)\vdots\vec{E}''^{(i)}(z,r,\omega)\cdot\left|\vec{E}''^{(i)}(z,r,\omega_a)\right|^2 d\omega_a \quad \text{(S9)}$$

In the derivation of eq.(S9) we have replaced $\vec{E}'(z,r,\omega)$ and $\vec{P}'^{(3,i)}(z,r,\omega)$ by $\vec{E}''^{(i)}(z,r,\omega)\times e^{-i(kz+\omega T_i)}$ and $\vec{P}''^{(3,i)}(z,r,\omega)\times e^{-i(kz+\omega T_i)}$ according to eqs.(S4) and (S5).

In addition, we have reduced the integration range [$-\infty,\infty$] to [0,∞] on the basis of the relation $\tilde{\chi}^{(3)}(\omega;\omega,\omega_a,-\omega_a)=\tilde{\chi}^{(3)}(\omega;\omega,-\omega_a,\omega_a)$ (the intrinsic permutation symmetry property of $\tilde{\chi}^{(3)}$). Similar to the conditions for $\chi^{(3)}(\omega_1;\omega_1,\omega_2,-\omega_2)$ and $\chi^{(3)}(\omega_2;\omega_2,\omega_1,-\omega_1)$ in eqs. (S7) and (S8) to be nonzero, $\tilde{\chi}^{(3)}(\omega;\omega,\omega_a,-\omega_a)$ in eq.(S9) is nonzero only when ω_a falls within the range [$\omega-\Omega_l-\Delta\Omega_l/2$, $\omega-\Omega_l+\Delta\Omega_l/2$] or [$\omega+\Omega_l-\Delta\Omega_l/2$, $\omega+\Omega_l+\Delta\Omega_l/2$]. In the following, we consider the situation that ω is positive and let ω_l and ω_h denote ω_a in the ranges [0,ω] and [ω,∞] respectively. Accordingly, we can rewrite eq.(S9) as

$$\vec{P}''^{(3,\mathrm{i})}(z,r,\omega)=2\varepsilon_0\times\left[\begin{array}{l}\int_0^{\omega}\tilde{\chi}^{(3)}(\omega;\omega,\omega_l,-\omega_l)\vdots\vec{E}''^{(\mathrm{i})}(z,r,\omega)\cdot\\ \left|\vec{E}''^{(\mathrm{i})}(z,r,\omega_l)\right|^2 d\omega_l\\ +\int_{\omega}^{\infty}\tilde{\chi}^{(3)}(\omega;\omega,\omega_h,-\omega_h)\vdots\vec{E}''^{(\mathrm{i})}(z,r,\omega)\cdot\\ \left|\vec{E}''^{(\mathrm{i})}(z,r,\omega_h)\right|^2 d\omega_h\end{array}\right]. \qquad \text{(S10)}$$

In order for $\vec{P}''^{(3,\mathrm{i})}(z,r,\omega)$ to be nonzero, ω_l within the range [$\omega-\Omega_l-\Delta\Omega_l/2$, $\omega-\Omega_l+\Delta\Omega_l/2$] needs to be covered in the spectrum of $\vec{E}''^{(\mathrm{i})}(z,r,\omega)$ with ω, or ω_h within the range [$\omega+\Omega_l-\Delta\Omega_l/2$, $\omega+\Omega_l+\Delta\Omega_l/2$] needs to be covered in the spectrum of $\vec{E}''^{(\mathrm{i})}(z,r,\omega)$ with ω. Note that $\tilde{\chi}^{(3)}(\omega;\omega,\omega_l,-\omega_l)$ equals $\tilde{\chi}^{(3)*}(\omega;\omega,\omega_h,-\omega_h)$ if ($\omega-\omega_l$) equals –($\omega-\omega_h$), similar to the relation $\chi^{(3)}(\omega_1;\omega_1,\omega_2,-\omega_2)=\chi^{(3)*}(\omega_2;\omega_2,\omega_1,-\omega_1)$ (see the paragraph below eqs.(S7) and (S8)). Given $\Delta\omega$ (5.5×10^{13} s^{-1}) considerably smaller than Ω_v (1.2×10^{14} s^{-1}, see Fig. 5 of the **Main Text**), we can hardly find ω_l within the range [$\omega-\Omega_v-\Delta\Omega_v/2$, $\omega-\Omega_v+\Delta\Omega_v/2$] or ω_h within the range [$\omega+\Omega_v-\Delta\Omega_v/2$, $\omega+\Omega_v+\Delta\Omega_v/2$] falling in the spectrum of $\vec{E}''^{(\mathrm{i})}(z,r,\omega)$ with ω. This signifies that $\vec{P}''^{(3,\mathrm{i})}(z,r,\omega)$ pertaining

to vibrational excitation via SRS tends to be zero. In other words, an 18 fs-laser pulse can barely excite the vibration.

By further substituting eq.(S10) into eq.(S6) we can deduce the wave equation

$$\frac{\partial \vec{E}''^{(\mathrm{i})}(z,r,\omega)}{\partial z} = -\frac{i2\pi k}{c\varepsilon_0} \times \begin{bmatrix} \int_0^{\omega} \tilde{\chi}^{(3)}(\omega;\omega,\omega_l,-\omega_l) \\ \cdot I'^{(\mathrm{i})}(z,r,\omega_l) \cdot \vec{E}''^{(\mathrm{i})}(z,r,\omega) d\omega_l \\ + \int_{\omega}^{\infty} \tilde{\chi}^{(3)}(\omega;\omega,\omega_h,-\omega_h) \\ \cdot I'^{(\mathrm{i})}(z,r,\omega_h) \cdot \vec{E}''^{(\mathrm{i})}(z,r,\omega) d\omega_h \end{bmatrix}. \quad \text{(S11)}$$

Here we have replaced $\left|\vec{E}''^{(\mathrm{i})}(z,r,\omega_{l(h)})\right|^2$ by $2\pi I'^{(\mathrm{i})}(z,r,\omega_{l(h)})/c\varepsilon_0$ according to eq.(5) in the **Main Text**. Subsequently, by expressing $\vec{E}''^{(\mathrm{i})}(z,r,\omega)$ as $\vec{A}^{(\mathrm{i})}(z,r,\omega)\times e^{-i\phi^{(\mathrm{i})}(z,r,\omega)}$ and thus $I'^{(\mathrm{i})}(z,r,\omega)$ as $c\varepsilon_0\left|\vec{A}^{(\mathrm{i})}(z,r,\omega)\right|^2/2\pi$, we can separate eq.(S11) into two terms, one for NLA and the other for NLR,

$$\frac{\partial I'^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega)}{\partial z'} = -2k \begin{bmatrix} \int_0^{\omega} \beta_l I'^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega_l) \times I'^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega) d\omega_l \\ -\int_{\omega}^{\infty} \beta_h I'^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega_h) \times I'^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega) d\omega_h \end{bmatrix} \quad \text{(S12)}$$

and

$$\frac{\partial \phi^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega)}{\partial z'} = k \begin{bmatrix} \int_0^{\omega} n_{2l} I'^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega_l) d\omega_l \\ +\int_{\omega}^{\infty} n_{2h} I'^{(\mathrm{i})}_{z_\mathrm{f}}(z',r,\omega_h) d\omega_h \end{bmatrix}. \quad \text{(S13)}$$

Note that in the derivation of eqs.(S12) and (S13) from eq.(S11), we have used $z=z_\mathrm{f}+z'$ with z' denoting the penetration depth of the i$^{\mathrm{th}}$ pulse into the sample and z_f representing the sample′s front surface position relative to the beam waist.

Here $\beta_{l(h)} \equiv -2\pi\tilde{\chi}^{(3)}_{\mathrm{Im}}(\omega;\omega,\omega_{l(h)},-\omega_{l(h)})/c\varepsilon_0$ and $n_{2l(2h)} \equiv 2\pi\tilde{\chi}^{(3)}_{\mathrm{Re}}(\omega;\omega,\omega_{l(h)},-\omega_{l(h)})/c\varepsilon_0$ are the third-order NLA and NLR coefficients. Since the range of ω_l for nonzero β_l and n_{2l} ([ω–Ω_l–$\Delta\Omega_l$/2, ω–Ω_l+$\Delta\Omega_l$/2]) and that of ω_h for nonzero β_h and n_{2h} ([ω+Ω_l–$\Delta\Omega_l$/2, ω+Ω_l+$\Delta\Omega_l$/2]) are of the same width ($\Delta\Omega_l$) and symmetrical about ω, we can fully derive β_h and n_{2h} from β_l and n_{2l} based on the relation $\tilde{\chi}^{(3)}(\omega;\omega,\omega_l,-\omega_l) = \tilde{\chi}^{(3)*}(\omega;\omega,\omega_h,-\omega_h)$ for (ω–ω_l)=–(ω–ω_h). Given any sample front surface position z_f, we can integrate eqs.(S12) and (S13) over the sample thickness z' from 0 to L to yield $I'^{(i)}_{z_f}(L,r,\omega)$ and $\phi^{(i)}_{z_f}(L,r,\omega)$ (equivalently $\vec{E}''^{(i)}_{z_f}(L,r,\omega)$ and $\vec{E}'^{(i)}_{z_f}(L,r,\omega) = \vec{E}''^{(i)}_{z_f}(L,r,\omega)\times e^{-i[k(z_f+L)+\omega T_i]}$) at the exit surface of the sample at z_f+L.

B. Simulation of the OKE signals

In this section we simulate the OHD-OKE signals of CS_2. In particular, we consider the contributions by nuclear motions but ignore that by electronic motion. As explained in ref.[18] of the **Main Text** the signal $I(\tau')$ is the convolution of the autocorrelation function $A_c(\tau')$ of the 18-fs laser pulses ($e^{-(\tau'/\tau)^2}$ with τ=18 fs) and the molecular nonlinear-response function $R(\tau')$,

$$I(\tau') \propto \int_{-\infty}^{\infty} A_c(t)R(\tau'-t)dt = A_c(\tau') * R(\tau'). \qquad \text{(S14)}$$

Here τ' is the delay time of the probe pulse relative to the pump pulse. $R(t)$ can be decomposed into $r_1(t)$ for diffusive relaxation, $r_2(t)$ for intermediate relaxation and $r_3(t)$ for libration (respectively named diffusive reorientation, polarizability distortion and libration in ref.[23] of the **Main Text**). They are respectively modeled as (ref. [18] of the **Main Text**)

$$r_1(t) = a_1 \exp\left(-\frac{t}{\tau_{\text{diff}}}\right)\left[1-\exp\left(-\frac{t}{\tau_{\text{rise1}}}\right)\right], \tag{S15}$$

$$r_2(t) = a_2 \exp\left(-\frac{t}{\tau_{\text{int}}}\right)\left[1-\exp\left(-\frac{t}{\tau_{\text{rise2}}}\right)\right] \tag{S16}$$

and

$$r_3(t) = a_3 \exp\left(-\frac{\alpha^2 t^2}{2}\right)\sin(\omega_0 t). \tag{S17}$$

In eqs.(S15)-(S17) the amplitudes are a_1=0.17, a_2=0.28 and a_3=0.55 with their sum normalized to 1. The relaxation time constants are τ_{diff}=1.68 ps and τ_{int}=0.4 ps. The rise time constants τ_{rise1} and τ_{rise2} are both assumed to be 140 fs. The reciprocal of the inhomogeneity is α=5.4 ps^{-1} and the principal frequency of libration is ω_0=6.72 ps^{-1}. By substituting these parameters into eqs.(S15)-(S17), we graphically show in frame (a) of Fig. S1 $A_c(\tau')*r_1(\tau')$, $A_c(\tau')*r_2(\tau')$, $A_c(\tau')*r_3(\tau')$, $A_c(\tau')*R(\tau')$ and $A_c(\tau')$ itself as functions of τ'. Because NLA and NLR induced in CS_2 by individual 18 fs-laser pulses via excitation of these molecular motions are only allowed to evolve within the pulse duration in this study, we pay special attention to the OHD-OKE signals at $\tau'\sim0$ and expand them in the range [–40 fs, 40 fs], as shown in frame (b). Accordingly, we see that the librational signal is considerably stronger than the signals of diffusive reorientation and polarizability distortion in the time extent [–40 fs, 40 fs].

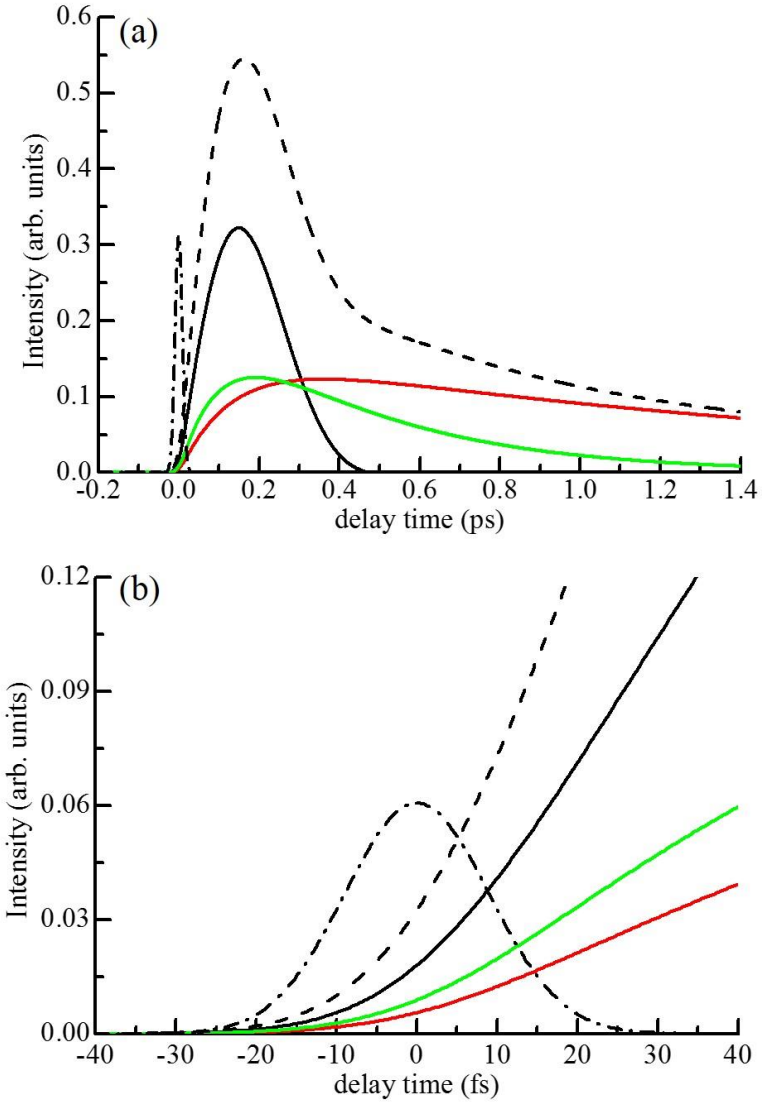

Fig. S1. (a) The convolutions of $A_c(\tau')$ and $r_1(\tau')$ (red line), $r_2(\tau')$ (green line), $r_3(\tau')$ (black line), $R(\tau')$ (dashed line), and $A_c(\tau')$ itself (dash-dotted line) exhibited as a function of τ' ranging between –0.2 and 1.4 ps. (b) Exhibition of the same convolution curves and a scaled down $A_c(\tau')$ (dash-dotted line) in a narrower delay time range [–40 fs, 40 fs].