Supporting Information for "Coherent Exciton Dynamics in Supramolecular Light-Harvesting Nanotubes Revealed by Ultrafast Quantum Process Tomography"

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1 TG experiment as a QPT

The basic idea of carrying out QPT using information from eight different TG spectra collected in the experiment has been intuitively explained in the main text. Here we elaborate on the formal details.

The three pulses interacting with the sample have carrier (center) frequencies $\omega_1, \omega_2, \omega_3$ which are close to the transition energies $\omega_{Ig} = \omega_{II,I} = \omega_{IO,O}$ or $\omega_{Og} = \omega_{OO,O} = \omega_{IO,I}$. We label the first, second, and third pulses as $p, q, r = \mathrm{I}, \mathrm{O}$, respectively, depending on whether they are centered close to ω_{Ig} or ω_{Og}. The pulses generate a third order time-dependent polarization which is detected by the reference pulse (fourth pulse) which, for our purposes, is ideally broadband, covering all the transitions of interest. Under this condition, the complex-valued *frequency-resolved* TG spectrum as a function of waiting time T and frequency ω can be immediately related to the half-sided Fourier transform of the complex-valued TG polarization $P_{k_s}^{pqr}(\tau = 0, T, t)$[1] *via*,

$$[S_{TG}]^{pqr}(\omega, T) = \int_0^\infty dt e^{i\omega t} P_{k_s}^{pqr}(\tau = 0, T, t). \tag{S1}$$

Here, τ (coherence time) and T (waiting time) correspond to the time intervals between the first and the second, and the second and the third pulses, respectively[2]. The free-induction decay time of the TG polarization is associated with t (sometimes known as echo-time). Since the half-sided Fourier transform in Eq. S1 is associated with this time interval, the set of emission frequencies in the TG spectrum $[S_{TG}]^{pqr}(T, \omega)$ corresponds to this free-induction decay. These frequencies are associated with the optical coherences between $|g\rangle$ and the SEM, or between the SEM and the DEM, and they correlate with the detection of different populations and coherences by the end of the waiting time. Consider the scenario where dissipative processes of these optical coherences are not spectrally broader than the separation between the different peaks in the TG spectra, which

[1] More precisely, the scalar $P_{k_s}^{pqr}$ is the projection of the TG polarization on the reference field, which is parallel to the axes of the nanotubes (as are the other pulses). Note the dual use of the word *polarization.* Here, it refers to the electric dipole density in the material, but we also use it to denote the direction of the electric field of the pulses.

[2] When $\tau \neq 0$, the TG experiment generalizes to the photon-echo configuration, which for our QPT purposes is not necessary.

is what happens in our case. Then, for purposes of QPT, one can properly define the integrated amplitude of the spectra across a specific spectral window of width $2\sigma_4 \equiv 330\,\mathrm{cm}^{-1}$ about the peak centered at a particular frequency ω_4[3],

$$\begin{aligned}[\bar{S}_{TG}]^{pqr}(\omega_4,T) &\equiv \int_{\omega_4-\sigma_4}^{\omega_4+\sigma_4} d\omega [S_{TG}]^{pqr}(\omega,T) \\ &= \int_{-\infty}^{\infty} dt \underbrace{\Theta(t)\sigma_4 \mathrm{sinc}\sigma_4 t e^{i\omega_4 t}}_{\equiv E_4^*(t)} P_{k_s}^{pqr}(\tau=0,T,t), \end{aligned} \tag{S2}$$

where we have used the step function $\Theta(t)$. The interpretation of Eq. S2 is quite intuitive and reads as follows: Integrating the broadband *frequency-resolved* complex amplitude $[S_{TG}]^{pqr}(T,\omega)$ across a spectral window $\omega \in [\omega_4-\sigma_4, \omega_4+\sigma_4]$ is equivalent to collecting the total TG photon-count signal arising from the overlap between an *effectively narrowband* reference pulse $E_4(t)$ (with carrier frequency ω_4 and time-width $\sim \sigma_4^{-1}$) centered at the end of the waiting time (at the same time as the third pulse r, at $t=0$) and the t dependent TG polarization $P_{k_s}^{pqr}$ undergoing free-induction decay. ω_4 is chosen to be resonant with one of the emission frequencies. E_4 is short in time (impulsive, broadband), meaning that σ_4 is wide enough to cover the dynamic broadening of a given optical transition. Yet, it is long in time (narrowband) enough to only be selective with respect to the different transitions. In previous articles, we have shown that a TG signal with four "impulsive-yet-selective" pulses prepares and detects populations and coherences in the SEM *via* the first two and the last two pulses in such a way that the TG experiment may be regarded as a QPT experiment. Hence, from Eq. S2, we conclude that QPT can also be achieved *via* the frequency-resolved TG spectra in this article.[1–3]

Fig. 3 in main text shows that the possible emission frequencies, and hence values of ω_4, in the different TG spectra are dictated by the third pulse r. If $r=O$, the induced TG optical coherence and therefore ω_4 take values close to $\omega_{Ig}=\omega_{II,I}=\omega_{IO,O}$ *via* SE and ESA, at $\omega_{Og}=\omega_{OO,O}=\omega_{IO,I}$

[3]The peaks are separated from one another by $\sim$330 cm^{-1} so windows of width 330 cm^{-1} are sufficiently narrow to detect single peak contributions, and broad enough to contain all the relevant spectral diffusion.

via GSB, SE, ESA, or GSR, or at $\omega_{OO,I}$ *via* ESA. Similarly, if $r = I$, ω_4 can take values close to $\omega_{II,O}$ *via* ESA, to $\omega_{Ig} = \omega_{II,I} = \omega_{IO,O}$ *via* GSB, SE ESA, or GSR, and $\omega_{Og} = \omega_{IO,I}$ *via* SE or ESA. Hence, for each of the eight frequency-resolved TG spectra $[S_{TG}]^{pqr}(\omega, T)$, there are three possible "carrier frequencies" ω_4 from which we can extract TG signals $[\bar{S}_{TG}]^{pqr}(\omega_4, T)$, yielding a total of 24 complex numbers as a function of T.

One can readily obtain explicit expressions for $[\bar{S}_{TG}]^{pqr}(\omega_4, T)$ by translating the double-sided Feynman diagrams in Fig. 3 in main text in terms of the initial states prepared by the first two pulses, and the final states detected by the last two pulses.[2–5] If $r = O$, these are,

$$
\begin{aligned}
[\bar{S}_{TG}]^{pqO}(\omega_4, T) \;=\; & C_{pqO} \overbrace{\mu_{pq}\mu_{qg}}^{\text{initial state preparation}} \\
& \times \begin{cases}
\underbrace{\overbrace{\mu_{Og}\mu_{Ig}}^{\text{final state detection}}}_{SE} \underbrace{\chi_{IOqp}(T)}_{} \underbrace{-\mu_{IO,I}\mu_{IO,O}\chi_{IOqp}(T)}_{ESA} & \text{for } \omega_4 = \omega_{Ig}, \\
\underbrace{\mu_{Og}^2\delta_{qp}}_{GSB} \underbrace{-\mu_{Og}^2\chi_{ggqp}(T)}_{GSR} & \\
\underbrace{+\mu_{Og}^2\chi_{OOqp}(T)}_{SE} \underbrace{-\mu_{OO,O}^2\chi_{OOqp}(T)}_{ESA} \underbrace{-\mu_{IO,I}^2\chi_{IIqp}(T)}_{ESA} & \text{for } \omega_4 = \omega_{Og}, \\
\underbrace{-\mu_{OO,O}\mu_{OO,I}\chi_{OIqp}(T)}_{ESA} & \text{for } \omega_4 = \omega_{OO,I},
\end{cases}
\end{aligned}
\tag{S3}
$$

and the analogous expressions hold for $[\bar{S}_{TG}]^{pqI}(\omega_4, T)$ upon the substitutions $O \to I$ and $OO \to II$. Here, we have highlighted the dipole transitions μ_{ij} associated with the initial state preparation and the final state detection in each case. We have also assumed that $\mu_{ij} = \mu_{ji}$ since the excitonic states can be taken to be real due to time-reversal symmetry. For the $\omega_4 = \omega_{Og}$ case, it is possible to simplify the expression by assuming that the total exciton population during the waiting time is distributed exclusively among $|O\rangle$, $|I\rangle$, and $|g\rangle$,

$$
\chi_{OOqp}(T) + \chi_{IIqp}(T) + \chi_{ggqp}(T) = \delta_{qp}, \tag{S4}
$$

so that it reads,

$$[\bar{S}_{TG}]^{pqO}(\omega_4,T) = C_{pqO}\mu_{pg}\mu_{qg}[(2\mu_{Og}^2-\mu_{OO,O}^2)\chi_{OOqp}(T)+(\mu_{Og}^2-\mu_{IO,I}^2)\chi_{IIqp}(T)] \text{ for } \omega_4=\omega_{Og}. \tag{S5}$$

This approximation relies on two assumptions: (a) That there are no uphill transfers of population to the DEM during the waiting time, which is very reasonable considering the large energy gap between the SEM and the DEM, and (b) that the transfer to the dark states is also negligible.

C_{pqO} indicates the joint transition probability amplitude to carry out the three different dipole transitions *via* the three different pulses. Whereas in principle one can obtain explicit expressions for this amplitude, in the present case, the narrowband pulses with imperfect Gaussian forms, the pulse overlaps, as well as the broadening of the TG transitions due to dynamic disorder altogether impede its precise determination. We shall write it as,

$$\begin{aligned} C_{pqO} &= f_{pq}E_p(\omega_{pg})E_q(\omega_{qg})E_O(\omega_{Og}) \\ &\approx f_{pq}\max(E_p(\omega))\max(E_q(\omega))\max(E_O(\omega)). \end{aligned} \tag{S6}$$

Here, we have used the fact that the pulses are narrowband and centered about the relevant transitions ($E_p(\omega_{pq}) \approx \max(E_p(\omega))$ and so on), and we extract the respective amplitudes from the power spectra of the pulses, $E_i(\omega) = \sqrt{|E_i(\omega)|^2}$ (assuming $E_i(\omega)$ has no chirp and its global phase is already considered in the phasing procedure with respect to the other pulses). We hide all the complexity of C_{pqO} in the complex-valued factor f_{pq} which takes into account the overlap between pulses p and q. Finally, from the absorption spectrum, we can get a good estimate of

$$\frac{\mu_{Og}}{\mu_{Ig}} \approx \sqrt{\frac{A(\omega_{Og})}{A(\omega_{Ig})}}, \tag{S7}$$

where $A(\omega)$ is the absorption spectrum of the material. Note that the contributions corresponding

to SE/GSB and ESA/GSR involve a net gain and loss of photons to the electric field in the k_s direction, respectively, and hence come with opposite signs. Also, GSB appears only if the first two pulses are resonant with the same transitions and therefore create a population (rather than a coherence) in the excited state, and hence, it is proportional to δ_{pq}. Since the GSB term monitors (stationary) ground state population during the waiting time T, it is proportional to $\chi_{gggg}(T) = 1$ and shows up as a T-independent background[4].

So far, we have 24 effective narrowband time (or frequency) integrated complex-valued TG signals $[\bar{S}_{TG}]^{pqr}(T,\omega)$ which amount to 48 real-valued data points as a function of T. Note that in general, these signals are linear combinations of different elements of $\chi(T)$ and, in fact, according to Eq. S3, several signals report on a single element of $\chi(T)$ at a time. Let us now count the number of elements of $\chi(T)$ to invert for our two-level system composed of $|I\rangle$ and $|O\rangle$. Hermicity of $\chi(T)$ requires that $\chi_{ijqp}(T) = \chi^*_{jipq}(T)$. This amounts to the real-valued population terms $\chi_{OOOO}(T)$, $\chi_{IIOO}(T)$, $\chi_{IIII}(T)$, and $\chi_{OOII}(T)$, and the complex-valued $\chi_{IOIO}(T) = \chi^*_{OIOI}(T)$, together with the non-secular (not energy conserving, also complex-valued) terms $\chi_{IOOO}(T) = \chi^*_{OIOO}(T)$, $\chi_{IOII}(T) = \chi_{IOII}(T)$, $\chi_{IOOI}(T) = \chi^*_{OIIO}(T)$, $\chi_{OOIO}(T) = \chi^*_{OOOI}(T)$, and $\chi_{IIIO}(T) = \chi^*_{IIOI}(T)$. Based on this symmetry, there are 16 real parameters of $\chi(T)$ to extract [5] out of a redundant set of 48 real-valued data points.

2 Energy level assignments

Energies of the SEM and DEM states addressed in our experiment have been self-consistently assigned from the frequency-resolved TG spectra. As a first examination, from the linear absorption, peak maxima corresponding to $|I\rangle$ and $|O\rangle$ are located at $\omega_{Ig} = 16695\,\mathrm{cm}^{-1}$ and $\omega_{Og} = 16970\,\mathrm{cm}^{-1}$, respectively. These peaks are broadened both by static and dynamic disorder of the

[4] This is not true if the pump pulses 1 and 2 prepare a nuclear wavepacket in $|g\rangle$ which is different from its initial equilibrium configuration.[6] This will not happen as long as the impulsive limit is satisfied and the Condon approximation is valid.

[5] Had the population stayed only in $|I\rangle$ and $|O\rangle$ (and not in $|g\rangle$ *via* GSR), the number of unknowns would have been reduced to 12 real parameters.[2,3]

ensemble. As shown in Fig. 2 in the main text, narrowband excitation in the experiment is effected in such a way that the pulses are centered at the edge of each band, therefore selecting only a subset of realizations of static disorder. Therefore, the average energies in the linear absorption do not coincide with those probed in the TG experiment. Hence, it is more accurate to extract the energy levels of interest from the TG spectra themselves, using the initial condition that no transfer processes have occured at $T = 0$,

$$\chi_{ijqp}(0) = \delta_{iq}\delta_{jp}. \tag{S8}$$

For instance, whereas the OOO spectrum can potentially contain three different emission frequencies, at $T = 0$ it consists of a single peak[6] with maximum amplitude at $\omega \sim 17068\,\mathrm{cm}^{-1}$. This peak must correspond to (see Eq. S3); also Fig. 3 in main text, left top panel) $\chi_{OOOO}(0) = 1$, in a combination of SE, ESA, and GSB processes. Whereas SE/GSB is expected to show up at $\sim$3.5 cm^{-1} red-shifted from ESA at cryogenic temperatures,[7] dynamic and some static disorder at room temperature forbids an unambiguous discrimination as it broadens peaks up to a total width of about 330 cm^{-1}, as mentioned at the beginning of SI, Sec. 1. From here, we infer that $\omega_{Og}, \omega_{OO,O} \sim 17068$ cm^{-1}. Analogously, from the III spectrum at $T = 0$ and $\chi_{IIII}(0) = 1$, we obtain $\omega_{Ig}, \omega_{II,I} \sim 16635\,\mathrm{cm}^{-1}$. Based on these observations, we use $\omega_{Og} = \omega_{OO,O} = 17068\,\mathrm{cm}^{-1}$ and $\omega_{Ig} = \omega_{II,I} = 16635\,\mathrm{cm}^{-1}$.

The presence of the SEM states $|I\rangle$ and $|O\rangle$ demand the consideration of an additional combination exciton $|IO\rangle$, which we treat as a doubly-excited state where the two excitons are present, one in $|I\rangle$ and the other in $|O\rangle$, and its energy is the sum of the two SEM exciton energies, $\omega_{IO,O} = \omega_{Ig}$ and $\omega_{IO,I} = \omega_{Og}$. This is a reasonable assumption considering that the interactions between the $|I\rangle$ and the $|O\rangle$ excitons will be weak across the 4 nm hydrophobic core separating them.

We confirm the extracted energies by analyzing the rest of the TG spectra at $T = 0$. First, OOI and IIO spectra each contain a single peak at 16572 and 17025 cm^{-1}, respectively. Due to the frequencies of the pulses involved in these two experiments, only GSB and ESA processes contribute at $\omega = \omega_{Ig} = \omega_{IO,O}$ and $\omega = \omega_{Og} = \omega_{IO,I}$, which is to a good approximation what we

[6] In fact, as we shall explain later, the two other potential peaks have negligible amplitudes even at $T > 0$.

see. Second, spectra IOI and OIO show peaks at 17012 and 16635 cm^{-1}, associated with SE and ESA at $\omega = \omega_{Og} = \omega_{IO,I}$ and $\omega = \omega_{Ig} = \omega_{IO,O}$. Finally, IOO and OII spectra show peaks at 17452 and 16118 cm^{-1} corresponding to ESA at $\omega = \omega_{OO,I}$ and $\omega = \omega_{II,O}$. These observations validate the energy assignments in Fig. 2b in main text.

3 Data processing and error analysis

As explained in SI Sec. 1, Fig. 3 in the main text and Eq. S3 comprehensively enumerate the possible processes within the SEM that can be detected from the eight different TG spectra. In principle, these processes manifest as three spectrally well-separated peaks in each TG spectrum, indicating general transfers amongst populations and coherences.

Figure 4 shows that the resulting set of signals is quite sparse, with signals at well-separated frequencies. We characterize the intensity of each peak by integrating the complex experimental spectra (real parts shown in Fig. 4) around the expected peak frequency using Eq. S2 with a half-width of $\sigma_4 = 165$ cm^{-1}. The TG emission bands are well separated by more than 330 cm^{-1}. Table S1 characterizes the total strength of the various signals by presenting the normalized contribution of $\sum_T \left|[\bar{S}_{TG}]^{pqr}(\omega_4, T)\right|^2$ for each frequency-resolved TG spectrum and choice of ω_4. Together with each entry, we have also indicated the elements of $\chi(T)$ associated with that signal. For instance, the peak centered at $\omega_{Og} = \omega_{OO,O}$ in the IIO spectra reports on both $\chi_{OOII}(T)$ and $\chi_{IIII}(T)$, whereas the peak at $\omega_{II,O}$ in OII is directly proportional to χ_{IOIO}. To obtain a rough idea of the experimental data, we have listed in bold the entries that contribute the most per TG spectrum, and most of them account for over 97% of the total norm of the respective experiment, which produces the sparse data set. The spectra such as IOO, where the dominant contribution is only 85%, clearly have lower signal-to-noise ratios, as can be seen in Fig. 4. We discuss the uncertainties resulting from this noise later in this section.

TABLE S1. Normalized contribution of $\sum_T |[\bar{S}_{TG}]^{pqr}(\omega_4,T)|^2$

TG spectrum\ω_4 [cm^{-1}]	$\omega_{Ig}=16635\,\mathrm{cm}^{-1}$	$\omega_{Og}=\omega_{OO,O}=\omega_{IO,I}=17068\,\mathrm{cm}^{-1}$	$\omega_{OO,I}=17501\,\mathrm{cm}^{-1}$
OOO	0.0001 (χ_{IOOO})	**0.9999** (χ_{OOOO}, χ_{IIOO})	0.0000 (χ_{OIOO})
IIO	0.0622 (χ_{IOII})	**0.9007** (χ_{OOII}, χ_{IIII})	0.0371 (χ_{OIII})
IOO	0.0320 (χ_{IOOI})	0.1231 (χ_{OOOI}, χ_{IIOI})	**0.8449** (χ_{OIOI})
OIO	**0.9973** (χ_{IOIO})	0.0018 (χ_{OOIO}, χ_{IIIO})	0.0009 (χ_{OIIO})
TG spectrum\ω_4 [cm^{-1}]	$\omega_{II,O}=16202\,\mathrm{cm}^{-1}$	$\omega_{Ig}=\omega_{II,I}=\omega_{IO,O}=16635\,\mathrm{cm}^{-1}$	$\omega_{Og}=17068\,\mathrm{cm}^{-1}$
OOI	0.0221 (χ_{IOOO})	**0.9779** (χ_{OOOO}, χ_{IIOO})	0.0000 (χ_{OIOO})
III	0.0050 (χ_{IOII})	**0.9947** (χ_{OOII}, χ_{IIII})	0.0003 (χ_{OIII})
IOI	0.0018 (χ_{IOOI})	0.0689 (χ_{IIOI}, χ_{OOOI})	**0.9294** (χ_{OIOI})
OII	**0.9886** (χ_{IOIO})	0.0061 (χ_{IIIO}, χ_{OOIO})	0.0052 (χ_{OIIO})

Note that the entries with small contributions correspond to nonsecular terms. This table serves as an illustration to the rationale behind our frequency-selective TG procedure, but it is not sufficient to extract $\chi(T)$, as the signals are weighted by dipole moment and electric field terms. To proceed in a more systematic fashion, we follow this procedure:

1. From each signal $[\bar{S}_{TG}]^{pqr}(\omega_4,T)$ in Eq. S3, construct the renormalized signal,

$$[\bar{s}_{TG}]^{pqr}(\omega_4,T)=\frac{[\bar{S}_{TG}]^{pqr}(\omega_4,T)}{\kappa_{pqr}}, \tag{S9}$$

   where $\kappa_{pqr}=\max[E_p(\omega)]\max[E_q(\omega)]\max[E_r(\omega)]\frac{\mu_{pg}\mu_{gq}}{\mu_{Ig}^2}$, with dipole ratios determined using Eq. S7.

2. Taking into account the initial condition Eq. S8 in Eqs. S9 and S5 as well as their analogues upon the $O\to I$ and $OO\to II$ substitutions, yields the following coefficients,

$$
\begin{aligned}
A &\equiv [\bar{s}_{TG}]^{OOO}(\omega_{Og},0) = f_{OO}(2\mu_{Og}^2 - \mu_{OO,O}^2),\\
B &\equiv [\bar{s}_{TG}]^{IIO}(\omega_{Og},0) = f_{II}(\mu_{Og}^2 - \mu_{IO,I}^2),\\
C &\equiv [\bar{s}_{TG}]^{OOI}(\omega_{Ig},0) = f_{OO}(\mu_{Ig}^2 - \mu_{IO,O}^2),\\
D &\equiv [\bar{s}_{TG}]^{III}(\omega_{Ig},0) = f_{II}(2\mu_{Ig}^2 - \mu_{II,I}^2),\\
E &\equiv [\bar{s}_{TG}]^{IOI}(\omega_{Og},0) = f_{IO}(\mu_{Ig}\mu_{Og} - \mu_{IO,I}\mu_{IO,O}),\\
F &\equiv [\bar{s}_{TG}]^{IOO}(\omega_{OO,I},0) = f_{IO}(\mu_{OO,O}\mu_{OO,I}),\\
G &\equiv [\bar{s}_{TG}]^{OIO}(\omega_{Ig},0) = f_{OI}(\mu_{Og}\mu_{Ig} - \mu_{IO,O}\mu_{IO,I}).\\
H &\equiv [\bar{s}_{TG}]^{OII}(\omega_{II,O},0) = f_{OI}(\mu_{II,I}\mu_{II,O}).
\end{aligned}
\tag{S10}
$$

These coefficients precisely constitute the set of dipole combinations required for the inversion of $\chi(T)$ from Eq. S3.

3. We arrange the coefficients from Eq. S10 into matrices,

$$\underline{\mathbb{M}}_{OO} = \underline{\mathbb{M}}_{II} \equiv \begin{bmatrix} 0 & 0 & G & -iG \\ A & B & 0 & 0 \\ 0 & 0 & F & iF \\ 0 & 0 & H & -iH \\ C & D & 0 & 0 \\ 0 & 0 & E & iE \end{bmatrix}, \underline{\mathbb{M}}_{OI} \equiv \begin{bmatrix} 0 & 0 & G & 0 & 0 & 0 & -iG & 0 \\ A & B & 0 & 0 & -iA & -iB & 0 & 0 \\ 0 & 0 & 0 & F & 0 & 0 & 0 & -iF \\ 0 & 0 & H & 0 & 0 & 0 & -iH & 0 \\ C & D & 0 & 0 & -iC & -iD & 0 & 0 \\ 0 & 0 & 0 & E & 0 & 0 & 0 & -iE \\ 0 & 0 & 0 & G & 0 & 0 & 0 & iG \\ A & B & 0 & 0 & iA & iB & 0 & 0 \\ 0 & 0 & F & 0 & 0 & 0 & iF & 0 \\ 0 & 0 & 0 & H & 0 & 0 & 0 & iH \\ C & D & 0 & 0 & iC & iD & 0 & 0 \\ 0 & 0 & E & 0 & 0 & 0 & iE & 0 \end{bmatrix}, \tag{S11}$$

and the signals into associated vectors,

$$\mathbb{S}_{OO}(T)=\begin{bmatrix}[\bar{s}_{TG}]^{OOO}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{OOO}(\omega_{Og},T)\\ [\bar{s}_{TG}]^{OOO}(\omega_{OO,I},T)\\ [\bar{s}_{TG}]^{OOI}(\omega_{II,O},T)\\ [\bar{s}_{TG}]^{OOI}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{OOI}(\omega_{Og},T)\end{bmatrix},\ \mathbb{S}_{II}(T)=\begin{bmatrix}[\bar{s}_{TG}]^{IIO}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{IIO}(\omega_{Og},T)\\ [\bar{s}_{TG}]^{IIO}(\omega_{OO,I},T)\\ [\bar{s}_{TG}]^{III}(\omega_{II,O},T)\\ [\bar{s}_{TG}]^{III}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{III}(\omega_{Og},T)\end{bmatrix},\ \mathbb{S}_{OI}(T)=\begin{bmatrix}[\bar{s}_{TG}]^{OIO}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{OIO}(\omega_{Og},T)\\ [\bar{s}_{TG}]^{OIO}(\omega_{OO,I},T)\\ [\bar{s}_{TG}]^{OII}(\omega_{II,O},T)\\ [\bar{s}_{TG}]^{OII}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{OII}(\omega_{Og},T)\\ [\bar{s}_{TG}]^{IOO}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{IOO}(\omega_{Og},T)\\ [\bar{s}_{TG}]^{IOO}(\omega_{OO,I},T)\\ [\bar{s}_{TG}]^{IOI}(\omega_{II,O},T)\\ [\bar{s}_{TG}]^{IOI}(\omega_{Ig},T)\\ [\bar{s}_{TG}]^{IOI}(\omega_{Og},T)\end{bmatrix} \tag{S12}$$

The goal is to extract $\chi(T)$, which is also written as a series of vectors,

$$\mathbb{X}_{OO}(T)\equiv\begin{bmatrix}\chi_{OOOO}(T)\\ \chi_{IIOO}(T)\\ \Re\{\chi_{OIOO}(T)\}\\ \Im\{\chi_{OIOO}(T)\}\end{bmatrix},\ \mathbb{X}_{II}(T)\equiv\begin{bmatrix}\chi_{OOII}(T)\\ \chi_{IIII}(T)\\ \Re\{\chi_{OIII}(T)\}\\ \Im\{\chi_{OIII}(T)\}\end{bmatrix},\ \mathbb{X}_{OI}(T)=\begin{bmatrix}\Re\{\chi_{OOOI}\}\\ \Re\{\chi_{IIOI}\}\\ \Re\{\chi_{OIOI}\}\\ \Re\{\chi_{IOOI}\}\\ \Im\{\chi_{OOOI}\}\\ \Im\{\chi_{IIOI}\}\\ \Im\{\chi_{OIOI}\}\\ \Im\{\chi_{IOOI}\}\end{bmatrix},$$

which fulfill,

$$\begin{aligned} \underline{\mathbb{M}}_{OO}\mathbb{X}_{OO}(T) &= \mathbb{S}_{OO}(T), \\ \underline{\mathbb{M}}_{II}\mathbb{X}_{II}(T) &= \mathbb{S}_{II}(T), \\ \underline{\mathbb{M}}_{OI}\mathbb{X}_{OI}(T) &= \mathbb{S}_{OI}(T). \end{aligned} \tag{S13}$$

Clearly, Eq. S13 can be written as a single matrix equation $\underline{\mathbb{M}}\mathbb{X}(T) = \mathbb{S}(T)$, where $\underline{\mathbb{M}} = \underline{\mathbb{M}}_{OO} \bigoplus \underline{\mathbb{M}}_{II} \bigoplus \underline{\mathbb{M}}_{OI}$ is a 24×16 matrix with each of the original matrices along the diagonal and zeros for the rest of the entries, i.e., it is of the block-diagonal form. $\mathbb{X}(T)$ and $\mathbb{S}(T)$ are the concatenations of the corresponding column vectors and have lengths 16 and 24, respectively. The condition number of $\underline{\mathbb{M}}$ is equal to 14.9, which indicates a well-behaved inversion, associated with the sparsity of the matrix.[7] A naive direct inversion of $\underline{\mathbb{M}}$ generally yields unphysical values of the process matrix $\chi(T)$. Using a semidefinite programming routine built using the CVX software,[8,9] we impose the positive-semidefinite constraint,

$$\sum_{ijqp} z_{iq}^{*} \chi_{ijqp}(T) z_{jp} \geq 0, \tag{S14}$$

for any complex-valued matrix z. This condition guarantees that the inverted $\chi(T)$ maps positive density matrices to other positive density matrices, as required for any physical χ. The result of this numerical procedure is given in Fig. 5 in main text, where most of the elements of $\chi(T)$ (namely, the nonsecular terms) result to be negligible.

Error analysis

We fit the dynamics encoded in $\chi(T)$ to functional forms shown in Table 1 in the main text, yielding the set of kinetic parameters τ_{OO}, β_{OO}, $\frac{2\pi}{\omega_{OI}}$, τ_{OI}, β_{OI}. Here we describe how the uncertainties in the extraction of the coefficients $X = \{A \ldots H\}$ in Eq. S10 affect the extracted kinetic parameters.

[7] The smaller the condition number, the more stable the inversion; since some signals are directly proportional to certain elements of $\chi(T)$, the matrix is sparse and the inversion is stable.

At $T = 0$, $\chi(T)$ must satisfy the initial condition of Eq. S8. Hence, most of the signals $[\bar{s}_{TG}]^{pqr}(\omega_4, 0)$ should vanish identically. This is not the case in practice, as there is always some experimental noise (see for instance, the IOO and IIO spectra in Fig. 4). Let us re-express the experimental spectra as $[\bar{s}_{TG}]^{pqr}(\omega_4, T) = [\bar{s}_{TG}]^{pqr}_{\text{ideal}}(\omega_4, T) + \delta^{pqr}_{\text{real}}(\omega_4, T) + i\delta^{pqr}_{\text{imag}}(\omega_4, T)$, where $\delta^{pqr}_{\text{real}}$ and $\delta^{pqr}_{\text{imag}}$ denote real-valued noise in the real and imaginary parts of the spectra. Recall from Eq. S2 and S9 that $[\bar{s}_{TG}]^{pqr}(\omega_4, T)$ is the result of an integral of $[S_{TG}]^{pqr}(\omega, T)$ over a window centered at ω_4. In practice, this operation is carried out as a discrete sum over $N = 58$ frequency pixels ω_i spanning a window of width $2\sigma_4$. We obtain the noise in $[\bar{s}_{TG}]^{pqr}(\omega_4, T)$ by assuming that the noise in $[S_{TG}]^{pqr}(\omega, T)$ for each frequency pixel is drawn from a normal distribution with zero mean and standard deviations $\sigma^{pqr}_{\text{real}}$ and $\sigma^{pqr}_{\text{imag}}$, independent of ω,T. We assume the noise distribution depends on the pulses used (pqr) and phase of the signal but otherwise does not vary in each experiment.

Since we assume that the noise has zero mean, for each dipole combination in the set $X = \{A \ldots H\}$, the best estimator of X_i is still the value given by Eq. S10. We can estimate the uncertainties in those values by finding $\sigma^{pqr}_{\text{real}}$, $\sigma^{pqr}_{\text{imag}}$.

We estimate $\sigma^{pqr}_{\text{real}}$, $\sigma^{pqr}_{\text{imag}}$ by looking at regions of the spectra where we know there should be no signal. For example, due to Eq. S8, at $T = 0$, $[S_{TG}]^{OOO}_{\text{ideal}}(\omega, 0)$ must vanish for values of ω_i in $[\omega_4 - \sigma_4, \omega_4 + \sigma_4]$ for $\omega_4 = \omega_{Ig}, \omega_{OO,I}$, so only the noise survives in those spectral regions. Our best estimator of $\sigma^{pqr}_{\text{real}}$ (which we will simply call $\sigma^{pqr}_{\text{real}}$) is given by the mean-square fluctuations. For example, for the OOO spectrum,

$$\begin{aligned}
\left(\sigma^{OOO}_{\text{real}}\right)^2 &= \frac{1}{2N}\sum_i \left(\Re[S_{TG}]^{OOO}(\omega_i, 0)\right)^2, \\
\left(\sigma^{OOO}_{\text{imag}}\right)^2 &= \frac{1}{2N}\sum_i \left(\Im[S_{TG}]^{OOO}(\omega_i, 0)\right)^2.
\end{aligned}$$

where the sum if over the $2N$ pixels contained in the two windows of frequencies centered at $\omega_4 = \omega_{Ig}, \omega_{OO,I}$.

These experimental uncertainties in each data point imply a normal distribution for each of

the dipole combinations in the set X; we expect that rerunning the experiment would give values for X chosen from those distributions. Our best estimate of the mean of that distribution is the value determined from Eq. S10. The best estimate of the standard deviation is, after collecting the relevant prefactors due to the discretization of the integral in Eq. (S2) and the definition in Eq. (S9), e.g., $\Sigma^A_{\text{real}} = \Delta_\omega \sqrt{N} \sigma^{OOO}_{\text{real}} / \kappa_{OOO}$, $\Sigma^A_{\text{imag}} = \Delta_\omega \sqrt{N} \sigma^{OOO}_{\omega\text{imag}} / \kappa_{OOO}$, where $\Delta_\omega = 5.8\,\text{cm}^{-1}$ is the size of a pixel in the TG spectra. The analogous procedure can be carried out for the rest of the coefficients B to H, giving the result in Table S2.

TABLE S2. Estimated values and uncertainties of the coefficients A to H

X	A	B	C	D
value/A	1	$0.003 + 0.021i$	$-0.147 + 0.097i$	$-0.100 - 0.094i$
$\Sigma^X_{\text{real}}/\lvert X\rvert$	0.0013	0.0777	0.0064	0.0244
$\Sigma^X_{\text{imag}}/\lvert X\rvert$	0.0063	0.0128	0.1454	0.0041
X	E	F	G	H
value/A	$0.036 - 0.056i$	$0.013 - 0.004i$	$-0.035 - 0.108i$	$0.045 - 0.038i$
$\Sigma^X_{\text{real}}/\lvert X\rvert$	0.0214	0.0643	0.0104	0.0035
$\Sigma^X_{\text{imag}}/\lvert X\rvert$	0.0292	0.1165	0.0190	0.0132

We propagate these uncertainties in the dipole combinations $A \ldots H$ to uncertainties in the kinetic parameters by creating empirical distributions for the kinetic parameters. We choose values for $X = \{A \ldots H\}$ from the normal distributions described by Table S2. For each such set X, we invert $\chi(T)$ and extract the kinetic parameters by best fit. We repeat this process 1000 times to create an implied distribution for the kinetic parameters, giving an estimate of their uncertainties due to the experimental noise effects on the dipole parameters. The mean of these distributions is the value determined using the parameters from Eq. S10, $\tau_{OO} = 212\,\text{fs}$, $\beta_{OO} = 3.3\,\text{fs}$, $\frac{2\pi}{\bar{\omega}_{OI}} = 70\,\text{fs}$, $\tau_{OI} = 155\,\text{fs}$, $\beta_{OI} = 2.6$. We take the standard deviations (e.g., $\Delta_{\tau_{OO}}$) of these distributions as a measure of the uncertainty of the uncertainty in the kinetic parameters. The result is that the kinetic parameters are best estimated to have uncertainties at 95% confidence interval due to the noise in the spectra of $1.96\Sigma(\tau_{OO}) = 5\,\text{fs}$, $1.96\Sigma(\beta_{OO}) = 0.2$, $1.96\Sigma(\frac{2\pi}{\omega_{OI}}) = 0.1\,\text{fs}$, $1.96\Sigma(\tau_{OI}) = 4\,\text{fs}$,

$1.96\Sigma(\beta_{OI}) = 0.2$. In addition to these uncertainties are the curve-fitting uncertainties due to disagreement between $\chi(T)$ and the functional forms of the fits. Table 1 of the main text reports two uncertainties for each parameter. The first is the curve-fitting uncertainty and the second is the signal-to-noise uncertainty producing errors in the estimates of the dipoles $A \ldots H$. The small uncertainty values, together with the small condition number of $\mathbb{M}$, indicate that the inversion of $\mathbb{X}(T)$, the extraction of kinetic parameters, and the entire QPT procedure are robust.

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