

Nonlinear Order Separation in Two-Dimensional Electronic Spectroscopy Quantifies Properties of Higher-Excited States

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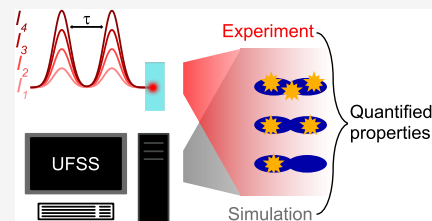


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ABSTRACT: Two-dimensional (2D) spectroscopy combines high temporal and spectral resolution, allowing the observation of ultrafast energy transfer and the separation of homogeneous and inhomogeneous broadening. Typically, 2D spectroscopy is dominated by the lowest-order nonlinear signal for a given phase-matching configuration, while signals of higher order are present but difficult to access separately. Recently, we introduced a technique to separate nonlinear orders in 2D spectroscopy by systematically varying the intensity of the pump pulses and postprocessing appropriately. Here, we unravel the full potential of higher-order 2D spectroscopy by separating multiple nonlinear orders at different multiquantum positions. As an example, we investigate a squaraine dimer. Using a theoretical model, we find excellent qualitative and quantitative agreement throughout all nonlinear orders and multiquantum positions. Our simulations demonstrate the sensitivity and information content hidden in the higher-order spectra such as transition dipole moments and energy levels even of highly excited states. Our results pave the way for establishing higher-order spectroscopy as a unique extension of multidimensional spectroscopy, providing access to highly excited states and their properties encoded in successive orders of nonlinearity.



Two-dimensional (2D) spectroscopy is an established method that combines ultrafast temporal resolution and multidimensional spectral information.^{1,2} As a generalization of transient absorption (TA) with resolution along both excitation- and detection-frequency axes, 2D spectroscopy is frequently used to investigate dynamics of processes in complex quantum systems. Examples include, but are not limited to, energy transfer processes in photosynthetic systems,^{3–7} coherences between states,^{8,9} chemical reactions,^{10,11} charge-transfer state dynamics,¹² singlet fission processes,¹³ and many more, as summarized in several review articles.^{14–20} One of the key features of 2D spectroscopy is the separation of signal contributions such as ground-state bleach (GSB), stimulated emission (SE), and excited-state absorption (ESA) along the excitation and detection axes, allowing the dynamics and properties of individual excited states to be probed.

A frequent problem in spectroscopic experiments is to find a balance between a sufficient signal-to-noise ratio (SNR) and overlapping higher-order contributions. The most commonly used TA and 2D experiments investigate third-order signals, in which the pump pulses interact twice with the system and the probe once,^{1,21} an increase in pump intensity leads to better SNR but also increases higher-order contributions originating from more than two interactions with the pump pulses. These higher-order signals overlap with the desired third-order signal.^{22–24} Higher-order contributions contain new information that is not part of a common third-order 2D spectrum, such as exciton–exciton interaction^{25,26} and properties of

higher-excited states.^{27–29} However, because the lower-order and higher-order signals are mixed, such information is difficult to extract. Multiquantum 2D spectroscopy experiments have signals whose lowest-order contributions result from more than two interactions with an excitation pulse, but contributions by even higher orders in nonlinearity can still contaminate the desired signal.^{29–32} The difficulty of separating higher-order signals and accounting for their contributions is a common challenge in spectroscopy, regardless of technique or sample.

We solved this longstanding problem in pump–probe spectroscopy such as TA by introducing the technique of intensity cycling, which systematically separates the nonlinear orders of response by using linear combinations of measurements at several excitation intensities.^{33–35} Recently, we generalized that approach and demonstrated that variation of the intensity of the excitation pulses allows nonlinear higher-order contributions to be extracted in 2D spectroscopy and related techniques.³⁶ The now separable nonlinear order responses contain spectral and dynamical information about both singly^{28,36} and multiply^{28,33} excited states. However, it is

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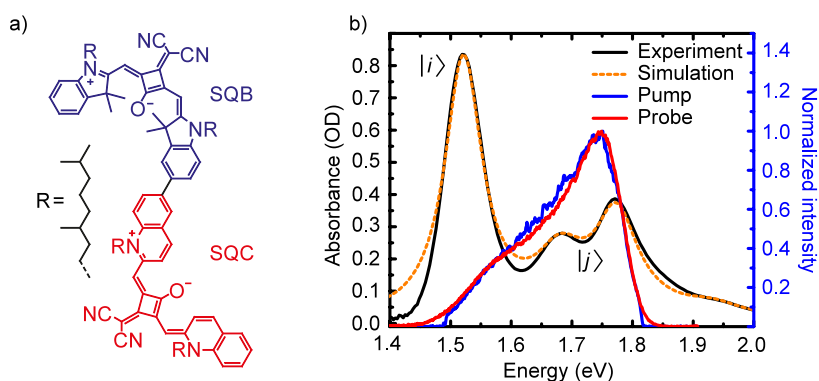


Figure 1. Characteristics of the investigated squaraine dimer dSQBC. (a) Molecular structure of dSQBC with the SQB part in blue and the SQC part in red. (b) Experimental (black line) and simulated (orange, dashed line) absorption spectra in toluene; pump (blue) and probe (red) laser spectra.

an open question what types of information one can extract from such higher-order spectra and to what extent quantitative information about quantum-mechanical properties can be determined. In the past, the presence of various artifacts, such as the uncontrolled presence of higher orders, often precluded a quantitative analysis for complex systems.

In this work, we show how single-quantum and double-quantum 2D electronic spectra, resolved into the various orders of nonlinear response, can be analyzed quantitatively by comparing accurate experiments and simulations. Specifically, we obtain high-order 2D spectra of a squaraine dimer and compare them to simulations that include the effects of the experimental pulse shape. The removal of artifacts arising from higher orders allows us to obtain quantitative insight. From the linear absorption and third-order response, we retrieve energy levels, relative dipole couplings of the singly excited states, and biexciton binding energies. From the higher orders, we determine the couplings of the single-exciton states to the doubly excited states. We thus produce a well-constrained model of this exemplary dimer. This work demonstrates the route to quantitative analysis of 2D electronic spectra.

We extract nonlinear orders through intensity variation across different n -quantum (nQ) positions in the 2D spectra. With noncollinear pulses, the nQ signals are detected in the $-n\vec{k}_1 + n\vec{k}_2 + \vec{k}_3$ direction. Here, we use a multidimensional experiment in the pump–probe geometry with $\vec{k}_1 = \vec{k}_2$, and thus all nQ signals are emitted in the same phase-matching direction. However, the signals can be separated along the ω_τ axis, where τ is the delay between pump pulses; the nQ spectra appear centered at $\omega_\tau = n\omega_0$, where ω_0 is the central frequency of the excitation pulses.³⁵ The lowest-order contributions to the nQ spectra are of $2n^{\text{th}}$ order in the pump pulse amplitudes. To separate nonlinear orders at all nQ positions, we first determine the optimal set of pump intensities, following the procedure described by Krich et al.³⁶ The 2D measurements are then taken for the optimized intensity steps and the resulting 2D data are used to isolate the signals of different orders of nonlinear response.

To demonstrate the principle experimentally, we dissolved a squaraine dimer, dSQBC, which is composed of an SQB and an SQC monomer (molecular structure shown in Figure 1a), in toluene.³⁷ Figure 1b shows the absorption spectrum in black, as well as the pump and probe spectra in blue and red, respectively. For comparison, Figure 1b also shows the simulated linear absorption, described below, as a dashed

orange line. The experimental linear spectrum consists of a large peak at 1.52 eV and two overlapping peaks at 1.68 and 1.78 eV. The peak at 1.52 eV corresponds to a transition to an excitonic state in the vibrational ground state, which we will call $|i\rangle$, while the two overlapping peaks indicate a vibronic mixture. This second exciton species will be referred to as $|j\rangle$. The squaraine dimer dSQBC shows slight changes in the relative peak strength for different sample concentrations, as seen in Supporting Information, Figure S10. For the simulations, we do not take this behavior into account, as the effects are minimal and larger aggregation effects can be ruled out, as there are no energetically shifted peaks in the differently concentrated spectra. The pump and probe spectra have identical shapes and cover all three peaks of the absorption spectrum. Due to the asymmetric shape of our laser spectra, the excitation intensity is enhanced at the blue edge of the absorption spectrum.

For the intensity-varied measurements we can define the electric field at time t and position $\vec{r}$ produced by the three pulses in the 2D measurement as

$$\vec{E}(t, \vec{r}) = \sum_{l=1}^3 \lambda_l \vec{e}_l \epsilon_l(t - t_l - \frac{\vec{k}_l \cdot \vec{r}}{\omega_l}) e^{-i(\omega_l(t-t_l) - \vec{k}_l \cdot \vec{r})} + \text{c.c.} \quad (1)$$

where ϵ_l describes the complex pulse envelope, including any chirp, ω_l the central frequency, t_l the arrival time, and $\vec{e}_l$ the polarization of the pulse number l . The scaling factor λ_l allows varying the amplitude while leaving all other pulse parameters unchanged. For our intensity-varied measurements, λ_3 is always 1 for the probe pulse and $\lambda_1 = \lambda_2 \equiv \lambda$ for the pump pulses. We then define the dimensionless intensity $I = \lambda^2$ that describes the simultaneous scaling of the amplitudes of the excitation pulse pair. The 2D spectroscopy signal $S(\tau, T, t, I)$ can then be written as

$$S(\tau, T, t, I) = \sum_{m=1}^{\infty} S^{(2m+1)}(\tau, T, t) I^m \quad (2)$$

where τ and T are the interpulse delays.³⁶ Here, $S(\tau, T, t, I)$ is the intensity-dependent signal and $S^{(2m+1)}(\tau, T, t)$ is the signal that is of $2m^{\text{th}}$ order in the excitation-pulse amplitudes. Since λ scales the excitation-pulse amplitudes and $I = \lambda^2$, the $S^{(2m+1)}$ signals are scaled by I^m because the excitation-pulse amplitudes interact $2m$ times. As shown elsewhere,³⁶ we can

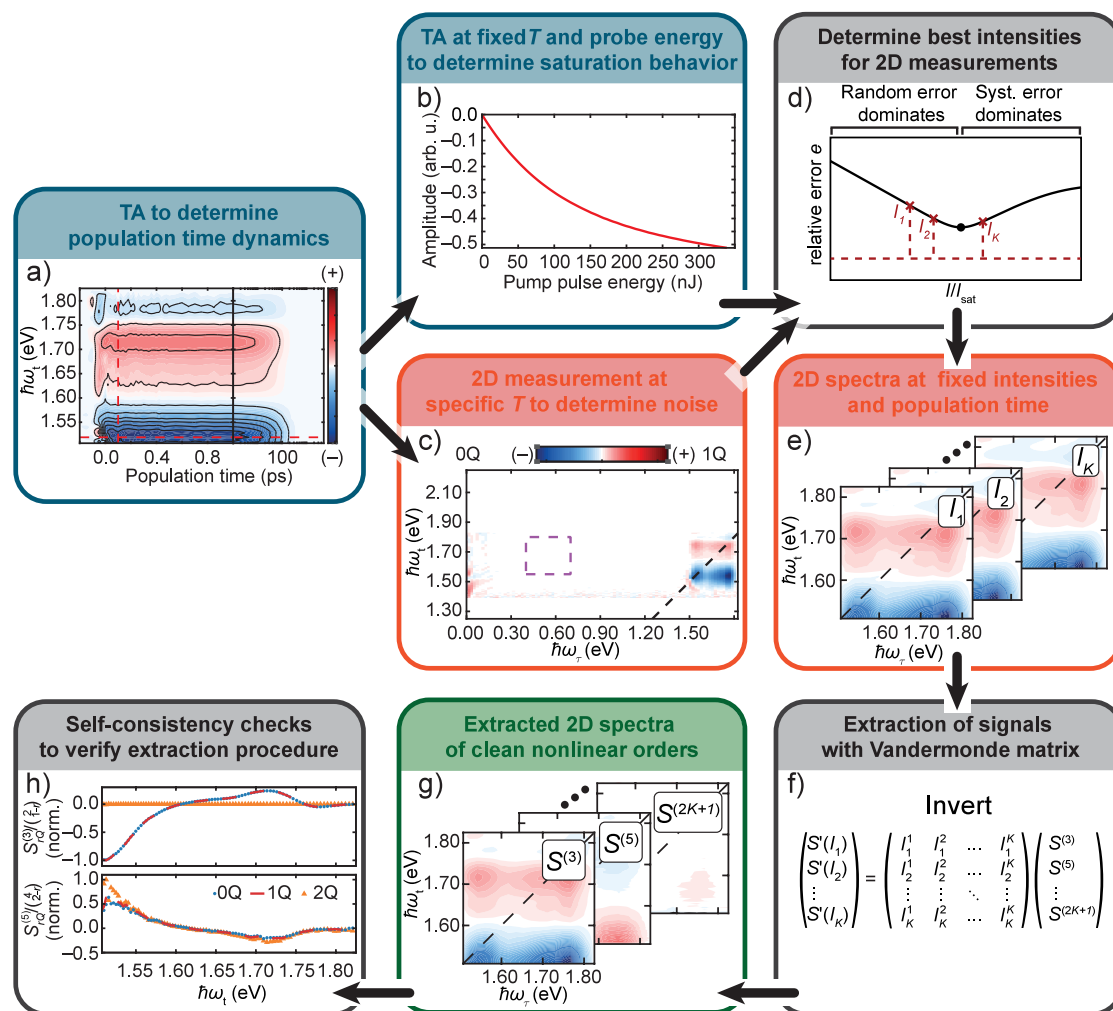


Figure 2. Scheme showing the experimental and data processing steps to separate signals of different orders of response. TA measurements are shown as blue boxes, 2D measurements as red boxes, data analysis steps as gray boxes, and the extracted 2D data as a green box. (a) TA measurement to determine the population time dynamics. (b) Intensity-dependent TA measurement at fixed $T = 100$ fs and probe energy $\hbar\omega_i = 1.51$ eV to characterize the saturation behavior. (c) Determination of the noise level in the region marked by the purple square far from any signal in the 2D spectrum at $T = 100$ fs. (d) Minimization of the relative error to determine the best intensities. (e) 2D spectra at optimal intensities and $T = 100$ fs. (f) Vandermonde matrix to extract signals from intensity-varied data. (g) Extracted 2D spectra of clean nonlinear orders. (h) Integrated signals of different nonlinear orders at rQ positions as self-consistency checks to verify extraction procedure.

extract the first K orders in eq 2 by measuring $S(\tau, T, t, I)$ with K different values of I and truncating the sum at an upper limit of $m = K$ instead of $m = \infty$. This truncation produces a systematic error, originating from the terms $S^{(2m+1)}$ for $m > K$. This systematic error can be estimated, and therefore the total error consisting of the random error and the systematic error can be minimized by an appropriate choice of K excitation intensities $\{I_k\}$. In this work, we use the same experimental procedure as in the proof-of-principle study on another sample³⁶ but then focus on how quantitative information about the system can be extracted when accurate experiments and simulations are combined.

Figure 2 shows an overview of the steps necessary to extract the nonlinear signals. In the first step, we analyzed the population-time dynamics in a TA experiment to determine what population time to use in our intensity-varied 2D measurement. In general, our method also works for experiments with multiple population times. However, to keep the measurement time short and decrease any potential influence from laser instabilities during the measurement, we

decided to only analyze 2D data from a single population time. We used a weak probe beam (with an intensity of a fourth of the lowest pump intensity), so the probe only interacts once. Figure 2a shows the TA measurement of dSQBC. From this measurement, we chose a population time of 100 fs, marked by the vertical red dashed line in Figure 2a, because the TA signal exhibits a maximum signal intensity at around 100 fs and pulse overlap effects are no longer present at this population time in the 2D measurements. Furthermore, time-dependent 2D measurements also showed that the 2Q signal displays its maximum signal intensity at 100 fs. The early time dynamics of the TA signal are shown in more detail in Supporting Information, Figure S1.

In the next steps, the ideal intensities for the extraction of response orders in the 2D spectra were determined. First, an estimate of the systematic error in the 2D spectra was obtained by studying the saturation behavior of the sample in an intensity-dependent TA measurement,³⁶ based on the fact that the TA spectrum is the excitation-frequency integral of the 2D spectrum according to the projection-slice theorem.³⁸ A TA

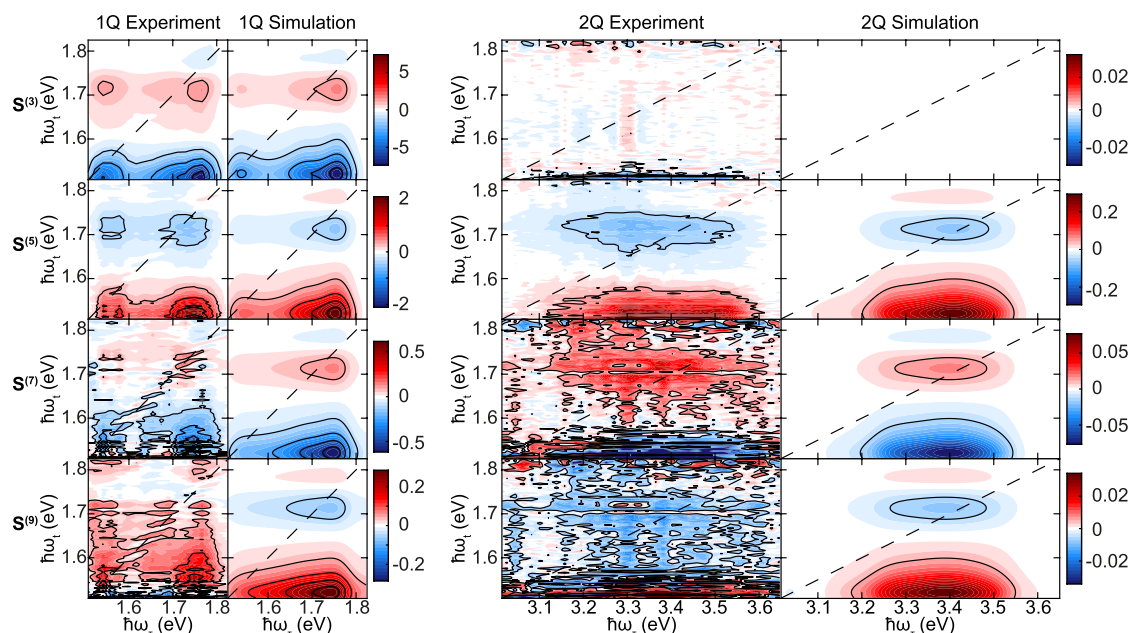


Figure 3. Separated experimental and simulated 2D spectra of different nonlinear orders and quantum positions at the population time $T = 100$ fs. The numbers in the color bar represent absorbance changes in mOD. The two left columns show the experiment and simulation of the 1Q maps, while the two columns on the right the experimental data and simulations for the 2Q signal. Each row represents a signal of a specific nonlinear order from $S^{(3)}$ (top) to $S^{(9)}$ (bottom). The dashed lines indicate the diagonals at $\hbar\omega_\tau = \hbar\omega_i$ (1Q) and $\hbar\omega_\tau = 2\hbar\omega_i$ (2Q).

experiment (Figure 2b) was measured with pump intensities ranging from 0.4 nJ to 339 nJ, with the spatial and temporal envelope of the pump held constant, so that the intensity and energy of the pulse were proportional. The intensity-dependent TA signal S^{TA} was fitted using the exponential saturation form

$$S^{\text{TA}}(T, \omega_i, I) = -S_{\text{max}}(T, \omega_i)(1 - e^{-I/I_{\text{sat}}(T, \omega_i)}) \quad (3)$$

where $S^{\text{TA}}(T, \omega_i, I)$ is the TA signal at population time T , frequency ω_i , and pump intensity I , and S_{max} and I_{sat} are sample- and pulse-dependent characteristics of the saturation form. From this fit, shown in more detail in Supporting Information, Section S3, we retrieved the values of $I_{\text{sat}} = 124$ nJ and $S_{\text{max}} = 0.53$ at $T = 100$ fs and $\omega_i = 1.51$ eV, which we used to estimate the systematic error in 2D measurements.

We also must quantify the noise level in the 2D measurements to find the optimal excitation intensities. To determine the noise level, a 2D measurement was taken at the population time $T = 100$ fs, and the noise level was determined far from any expected signal, in the region of interest marked by the purple square on the 2D map in Figure 2c. For our measurement a value of 5×10^{-7} was calculated for the standard deviation of the noise following the procedure outlined in the Supporting Information of our previous work.³⁶

At this point, both main sources of error were known: systematic error due to saturation behavior and random error due to noise in the 2D measurement. The combination of these two types of error was then used to calculate the optimal pump intensities to minimize the relative error in the extracted orders (Figure 2d). In our case, the experimental setup limited the maximum possible intensity of the excitation pulse to 15 nJ, which led to an ideal number of intensity steps as described earlier.³⁶ From the error analysis, four ideal intensities were determined, corresponding to pump pulse energies of 1.74 nJ, 7.35 nJ, 12.9 nJ, and 15 nJ. These are

optimal for minimizing the error in the first three nonlinear orders $S^{(3)}$, $S^{(5)}$, and $S^{(7)}$, at both 1Q and 2Q positions. Code for finding the optimal intensities is freely available on GitHub.³⁹

The 2D measurements were then performed at the four ideal intensities calculated and the chosen population time (Figure 2e). The complete 2D maps are shown in Supporting Information, Figure S4. The nonlinear orders were then extracted at each ω_τ and ω_i by inversion of the equation

$$\begin{pmatrix} S(I_1) \\ S(I_2) \\ S(I_3) \\ S(I_4) \end{pmatrix} = \begin{pmatrix} I_1 & I_1^2 & I_1^3 & I_1^4 \\ I_2 & I_2^2 & I_2^3 & I_2^4 \\ I_3 & I_3^2 & I_3^3 & I_3^4 \\ I_4 & I_4^2 & I_4^3 & I_4^4 \end{pmatrix} \begin{pmatrix} S^{(3)} \\ S^{(5)} \\ S^{(7)} \\ S^{(9)} \end{pmatrix} \quad (4)$$

which is the truncated form of eq 2 with $K = 4$. The 2D spectra of nonlinear orders up to $S^{(9)}$ were extracted and are shown in Figure 2g.

In the final step of the extraction and measurement procedure, self-consistency checks were performed comparing the n Q signals located at different positions in the 2D spectrum;³⁶ for our experiment we compared the signals at the 0Q, 1Q, and 2Q positions (Figure 2h). The $S^{(3)}$ signals at the 0Q and 1Q positions show excellent agreement, and the $S^{(3)}$ 2Q signal shows no signal amplitude, as expected, since the lowest nonlinear signal contributing at the 2Q position is $S^{(5)}$. For the $S^{(5)}$ signal, the integrated and scaled signals at all three n Q positions show good agreement, only showing some minor disagreement at the edge of the excitation spectrum. These self-consistency checks are shown in more detail in Supporting Information, Section S5; they give a good indication that the extracted orders $S^{(3)}$ and $S^{(5)}$ are of high quality, with minimal contamination error.

We can now analyze the isolated spectral orders. As expected, the $S^{(3)}$ spectrum at the 1Q position, shown in Figure 3 (top left), displays the same three peaks along the excitation-frequency axis as the linear absorption spectrum, but weighted by the pump intensity, which causes the highest-energy peak to be the strongest. The two higher-energy peaks visible in the linear absorption spectrum mostly merge in the nonlinear spectrum; we refer to the peaks between $\hbar\omega_\tau = 1.65$ and 1.8 eV as the $|lj\rangle$ peak and the lowest-energy peak at $\hbar\omega_\tau = 1.55$ eV $\equiv \hbar\omega_i$ as the $|li\rangle$ peak, corresponding to excitation of the lowest-energy exciton. Along the detection frequency axis, $S^{(3)}$ shows two distinct bands, a negative band between $\hbar\omega_t = 1.52$ and 1.60 eV and a positive band between $\hbar\omega_t = 1.65$ and 1.75 eV. The negative band indicates that it is dominated by GSB and SE connected to $|li\rangle$, while the higher-energy band is positive and dominated by ESA from $|li\rangle$ to the biexciton, which we label $|lij\rangle$. The ESA from $|li\rangle$ to $|lij\rangle$ is at nearly the same $\hbar\omega_i$ spectral position as the GSB of $|lj\rangle$.

The $S^{(3)}$ spectrum shows that excited populations have mostly relaxed to $|li\rangle$ before the probe arrives. The upper diagonal peak, corresponding to absorption and re-emission at $\hbar\omega_\tau = \hbar\omega_t = 1.76$ eV, is only barely visible, indicating that the higher-excited exciton has mostly decayed and no longer displays SE from that location. Similarly, the mid-diagonal peak at $\hbar\omega_\tau = \hbar\omega_t = 1.67$ eV is not visible at all. Cuts taken at different $\hbar\omega_\tau$ positions, depicted in Supporting Information, Figure S7, also show that the system has predominantly relaxed to the lowest single-excited state by 100 fs; the normalized linecuts overlap, indicating that even though different states are excited by the pump pulse, as seen by the multiple peaks along the ω_τ axis, the probe interacts mostly with one state, as the same energetic structure is visible for all cuts along the ω_t axis. The TA data shown in Supporting Information, Section S2, further support the conclusion that the system is mostly relaxed by $T = 100$ fs, and the SE appearing only at $\hbar\omega_t = \hbar\omega_i$ is consistent with emission coming from the lowest-energy exciton.

The ESA band near $\omega_t = \omega_i$ reveals the energy gap between $|li\rangle$ and $|lij\rangle$ and the strength of the transition dipole moment connecting $|li\rangle$ to $|lij\rangle$. The $S^{(3)}$ ESA band does not contain information about transitions to the doubly excited states from higher-energy singly excited states because they are not occupied. Information about the higher-lying singly excited states could be extracted from $S^{(3)}$ alone by considering smaller population times, which would involve detailed modeling of dynamics and might also require considering population times where pump and probe pulses overlap, which can be difficult.

The higher-order 1Q spectra (Figure 3, left column, second to fourth row) have the same peak structure as $S^{(3)}$ but with signs alternating as the order increases, with the band at higher ω_t obscured by noise for $S^{(7)}$ and $S^{(9)}$. This peak structure is consistent with the multiply excited states mostly having relaxed to the singly excited states, so there are no significant novel signals arising from multiply excited states. The relaxation of multiexcitons is consistent with the known fast time scale of exciton–exciton annihilation (EEA) in a similar SQAB dimer, which has a relaxation time of about 30 fs.^{27,40}

Similar observations can be made in the experimental data at the 2Q spectral position (Figure 3, third column). The $S^{(3)}$ signal is zero within the experimental error, at the 2Q position, which is expected since $S^{(5)}$ is the lowest order that can contribute at the 2Q position. The 1Q and 2Q $S^{(5)}$ signals have peaks at the same ω_τ . The 2Q signal, which in principle could

display emission and absorption at new spectral locations, displays only a single emission band and a single absorption band along $\hbar\omega_\nu$, just as the 1Q $S^{(5)}$ signal, again consistent with the system being mostly relaxed to the lowest-energy single exciton, even after double excitation. Similarly to the signal at the 1Q position, the sign of the signal flips on moving to $S^{(7)}$ and again to $S^{(9)}$. Unlike in the 1Q spectra, for the higher orders ($S^{(7)}$ and $S^{(9)}$), the signal near $\hbar\omega_t = 1.72$ eV is the most prominent, as the lower-energy feature is noisier.

We perform a more detailed analysis of the spectra by considering the long population time limit in which the system has fully relaxed to $|li\rangle$, regardless of the initial excitation number. We simulated spectra using the Ultrafast Spectroscopy Suite (UFSS).^{41,42} By learning the set of parameters in the model that are consistent with the linear and 2D spectra, we reveal the underlying physics of the dSQBC dimer. We demonstrate below how we can recover some of the information about the higher-lying excited states in the long-population-time limit by performing a detailed comparison of $S^{(3)}$ and $S^{(5)}$, rather than analyzing $S^{(3)}$ at smaller population times. That comparison works even when the system has reached quasi-equilibrium in the lowest-energy singly excited state, removing the need for detailed modeling of system dynamics.

Using UFSS, we simulated all the nonlinear orders observed experimentally at the 1Q and 2Q positions. We used a modified version of the model originally developed for the SQAB system.³¹ The model consists of two coupled monomers where each monomer consists of a three-level electronic system as described in more detail in Supporting Information, Section S1. Since the linear spectrum shows clear vibronic states, we modified the model to explicitly include two vibrational modes, one per site, in the Hamiltonian, whereas the other work³¹ treated all vibrations as a Markovian bath. We include the lowest six vibrational levels from each of the two vibrational modes, but we continue to treat the other modes as a Markovian bath. The pump spectrum strongly affects the peak heights in the 2D spectra, so obtaining quantitative agreement between simulations and experiment requires that these effects be included, which is a standard feature of UFSS.⁴¹ Therefore, all nonlinear signals were simulated using chirped pump pulses chosen to match the experimental intensity spectrum. We fit the experimental pulse intensity spectrum $I(\omega)$, found through a linear spectrally resolved intensity measurement, to the sum of five Gaussians and set $\tilde{e}(\omega)$ to the square root of the result. To quantify the chirp, we extract the group-delay dispersion (GDD) by fitting the spectral phase data retrieved through frequency-resolved optical gating (FROG) with a second-order polynomial. From the fit, we obtain a value of ± 36 fs² for the GDD. The sign is not known directly in second-harmonic-generation FROG. We chose the positive value for our simulations as described in more detail in Supporting Information, Section S10. Because the experimental results show that the system was mostly relaxed to the lowest-energy exciton before the probe arrived, we cannot determine the relaxation rates. Instead, simulations were performed at a fictitious population time large enough that all relaxation processes other than fluorescence (lifetime approximately 1.6 ns³¹) are complete. To determine the set of parameters in the model best describing our investigated sample dSQBC, we match simulated spectra to experimental spectra in three steps. First, we fix most of the static Hamiltonian and bath coupling

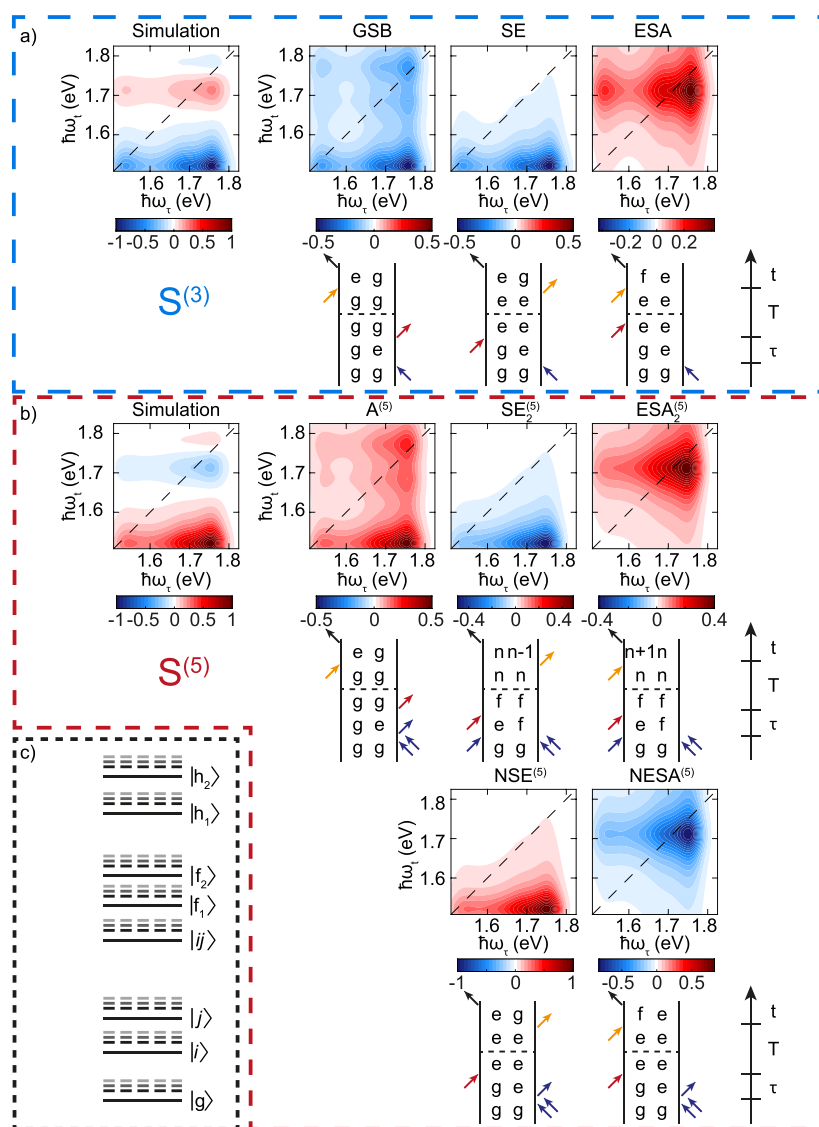


Figure 4. Separated simulated signal contributions and examples of corresponding double-sided Feynman diagrams. (a) $S^{(3)}$ signal and GSB, SE, and ESA signal contributions with exemplary corresponding double-sided Feynman diagrams. (b) $S^{(5)}$ signal and $A^{(5)}$, $SE^{(5)}$, $ESA^{(5)}$, $NSE^{(5)}$, and $NESA^{(5)}$ signal contributions with exemplary corresponding double-sided Feynman diagrams. (c) Energy scheme of the two coupled three-level systems representing the two monomer units.

parameters by reproducing the linear absorption spectrum. In the second step, we establish the transition dipole moment between exciton $|i\rangle$ and the biexciton $|ij\rangle$, as well as the biexciton binding energy, by matching the intensity ratio of the GSB and ESA regions in the third-order 1Q spectrum. In the last step the remaining unknown transition dipole moment is fixed by comparison of relative peak intensities between $S^{(3)}$ and $S^{(5)}$ signals. Steps one and two are described in more detail in [Supporting Information, Section S1](#) and step three in [Supporting Information, Section S6](#). No further fitting was performed. Consequently, the simulated seventh- and ninth-order spectra, as well as other features in the third- and fifth-order spectra constitute predictions of the model and are compared qualitatively with experiment without additional parameter adjustment. In [Figure 3](#), columns two and four show the simulated nonlinear orders. The computational orders are scaled so that the maximum of every order matches the maximum of the corresponding nQ experimental signal.

The simulations and experiments are in excellent agreement. Along the detection-frequency axis, we see the same two bands, one indicating GSB and SE connected to $|i\rangle$, the other indicating ESA from $|i\rangle$, as in the experiment. Further GSB peaks are overlapped by the ESA signal and are not distinguishable. For the higher orders, the locations of the peaks remain the same as in the lowest order, with the sign being inverted every second order, as in the experiment. This alternation is guaranteed in our simulations, since we have deliberately chosen a long population time in which the population is only in $|i\rangle$ when the probe arrives. The excellent agreement between the simulated and experimental peak heights could only be achieved by including the effects caused by the spectral shape of the electric field of the pump pulses. The excellent agreement in [Figure 3](#) between experiment and simulation demonstrates, on the one hand, that our model captures the underlying excitonic structure and processes contributing to the various nonlinear orders and, on the other hand, that the experimental separation into nonlinear orders

now opens the door for quantitative evaluations because artifacts from higher orders are removed.

The UFSS algorithm allows us to separate our simulated spectra into the underlying Liouville pathways, revealing which specific signal contribution is present for each peak at the various nonlinear orders. Parts a and b of Figure 4 show the simulated $S^{(3)}$ and $S^{(5)}$ 2D maps, respectively. The $S^{(3)}$ signal is divided into the usual contributions of GSB, SE, and ESA. The GSB signal is the negation of the absorption A, and the SE and ESA originate from singly excited states produced by pump excitation.²⁸ The $S^{(5)}$ signal can similarly be broken into five contributions: there are SE and ESA processes originating from doubly excited states produced by the pump, which we call $SE_2^{(5)}$ and $ESA_2^{(5)}$,²⁸ and three “negations” of the processes contributing to $S^{(3)}$. These negations are processes in which the system is in the same state after the pump pulses as in the analogous lower-order contributions, and the probe then interacts with the same state after the last pump interaction, but the sign is inverted with respect to $S^{(3)}$, analogous to the case of normal GSB that negates absorption. Here, for $S^{(5)}$, we call the negated contributions $A^{(5)}$ – since the negation of the GSB is a positive contribution to absorption –, negated SE (NSE), and negated ESA (NESA). The total $S^{(2m+1)}$ signal is normalized in Figure 4, so its maximum value is 1, and the contributions of the shown pathways sum up to the total.

Below each respective 2D map, we include an exemplary double-sided Feynman diagram. In these Feynman diagrams, $|g\rangle$, $|e\rangle$, and $|f\rangle$ correspond to the ground state, a singly excited state, and a doubly excited state, respectively. The state $|n\rangle$ can represent either a singly or a doubly excited state, depending on the completion of the exciton–exciton annihilation during the population time. All symbols on the left of each diagram represent ket vectors, while all symbols on the right represent bra vectors. In the diagrams, blue arrows indicate an interaction with the first pump pulse, red ones with the second pump pulse and orange ones with the probe pulse. Furthermore, $|n+1\rangle$ corresponds to $|n\rangle$ being excited, while $|n-1\rangle$ represents a state originating from a de-excitation of $|n\rangle$. The scheme in Figure 4c shows the excitonic states that result from the coupling of two monomers, each of which is set up as an electronic three-level system. In addition, the electronic states are coupled to two vibrational modes with six vibrational levels each, which are depicted as dashed lines. For better readability, not all vibronic states are included in the scheme.

We start by discussing what we can learn about the system when considering only the lowest-order spectrum $S^{(3)}$. The clear presence of the positive ESA band allows us to extract the biexciton binding energy and the dipole strength that connect the lowest-energy exciton to the biexciton. Extracting the biexciton binding energy is somewhat complicated because the $|j\rangle$ exciton is a vibronic doublet, so we cannot determine the bare biexciton energy simply by adding the excitation energies to $|i\rangle$ and $|j\rangle$. In addition, the GSB band for the $|j\rangle$ doublet spectrally overlaps with the ESA band. Our model includes a coupling K between the three doubly excited electronic states; K shifts the biexciton energy compared to independent excitations, which is the origin of biexciton binding in the model. We determine K from the position ω_i of the ESA band in $S^{(3)}$ and define the biexciton binding energy as the energy difference between the biexciton energy and the “bare” value obtained with $K = 0$. The ESA band at $\hbar\omega_i = 1.71$ eV shows the energy separation between $|i\rangle$ and $|ij\rangle$. Using our model, we

find that the binding energy of the $|ij\rangle$ biexciton is about 0.05 eV, and that the transition dipole moment is $\mu_{ij,i} \approx \mu_{ig}$ where g indicates the electronic ground state.

Since the excited populations in the simulations have relaxed to the exciton state $|i\rangle$ by the time the probe arrives, there are no clear spectral features related to the exciton $|j\rangle$ found in the simulated spectra; similarly, there are no signatures of the doubly excited states of higher energy because the corresponding ESA transitions from $|i\rangle$ are outside the spectral window of the probe. However, even though the system has fully relaxed to $|i\rangle$ when the probe arrives, there are still spectral signatures of the dipole strength connecting the exciton $|j\rangle$ to the doubly excited electronic states, which we can use to extract the ratio of the transition dipole moments. The key feature of the 1Q $S^{(5)}$ signal that we exploit is that the peaks along the ω_τ axis occur in the same frequency regions as the $S^{(3)}$ signal, but have different relative weights. The weight change occurs because the $S^{(5)}$ signal has contributions from the Liouville pathways that include two additional pump-induced transitions compared to the $S^{(3)}$ signal. For a subset of diagrams, these transitions occur between the singly and doubly excited states, and later relaxation of the population does not remove these effects. These diagrams are therefore imprinted with information about the dipole strength of various singly to doubly excited states. From the change in peak weights with ω_τ in $S^{(3)}$ and $S^{(5)}$ we can extract information on the pump-weighted average dipole strength,

$$d_e = \sqrt{\sum_f \mu_{fe}^2 I_{\text{pump}}(\omega_{fe}) / \sum_f I_{\text{pump}}(\omega_{fe})} \quad (5)$$

where e indicates a singly excited state (either $|i\rangle$ or $|j\rangle$), f indicates a doubly excited state, μ_{fe} is the dipole strength between them and $I_{\text{pump}}(\omega_{fe})$ is the pump intensity at the frequency difference between the two states.

To validate the agreement between simulation and experiment, we compared the ratio of peak intensities in two regions of ω_i : the GSB- and SE-dominated signal for $\hbar\omega_i$ between 1.51 and 1.60 eV and the ESA signal for $\hbar\omega_i$ between 1.67 and 1.75 eV. We integrated the signals between $\hbar\omega_\tau = 1.50$ and 1.62 eV for the peak corresponding to exciton $|i\rangle$ and between $\hbar\omega_\tau = 1.62$ and 1.82 eV for the peak corresponding to exciton $|j\rangle$. The regions of interest are shown in Supporting Information, Figure S8. The ratios were then calculated as

$$R_m = \frac{\text{Peak}_{i,S^{(m)}}}{\text{Peak}_{j,S^{(m)}}} \quad (6)$$

for $m = 3$ and $m = 5$. Our observable is the ratio of these ratios,

$$X = \frac{R_3}{R_5}, \quad (7)$$

which quantifies the difference in these normalized peak amplitudes between the $S^{(3)}$ and $S^{(5)}$ signals. We performed this analysis for both the ESA signal and the overlapping GSB and SE signals, giving us the two values X_{ESA} and $X_{\text{GSB,SE}}$, respectively.

We chose this procedure since the intramanifold relaxation of excitons is nearly complete at our measured population time, so cuts along ω_i at fixed ω_τ have approximately the same shape, with only the overall amplitude varying, as shown in Supporting Information, Figure S7. Simulations at shorter T show that such cuts vary along ω_τ but those variations

disappear when the system has relaxed to the $|l\rangle$ state before the probe arrives, which corresponds to our experimental condition. The amplitudes of these peaks at different ω_τ still contain information from excitation, which in the $S^{(5)}$ signals includes pathways that passed through doubly excited states, allowing us to determine d_j/d_i .

The ratio X is only an indirect measure of the ratio d_j/d_i , because there are many other pathways that contribute to the signal but do not depend on d_i or d_j . Experimentally, we find $X_{\text{ESA}} = 1.2$ and $X_{\text{GSB,SE}} = 1.3$. If the system were fully relaxed, these ratios would be identical, because both signals arise from a single excited state; these values being nearly equal is consistent with relaxation to the $|l\rangle$ exciton being nearly complete at $T = 100$ fs. In [Supporting Information, Section S11](#), we explore how residual $|j\rangle$ exciton population affects the X ratios. To compare X with simulation, we must find a set of parameters that is consistent with the linear absorption and $S^{(3)}$ spectra and then vary d_i and d_j within these constraints. The transition dipoles from the ground to the singly excited states are fixed by the linear absorption spectrum, and the $S^{(3)}$ spectrum fixes $\mu_{ij,p}$, leaving one free transition dipole parameter in our model. We vary this free parameter and simulate both $S^{(3)}$ and $S^{(5)}$ to determine the ratio $X_{\text{GSB,SE}}$, which is identical to X_{ESA} in the simulation due to the long population time limit, as shown in [Supporting Information, Section S6](#) in more detail. By matching the average experimental value of $X = 1.25$, we find that $d_j \approx 2d_i$. Since the experimental X ranges from $X_{\text{ESA}} = 1.2$ to $X_{\text{GSB,SE}} = 1.3$, we determine an error bound on d_j/d_i of about 5%. In addition, the ratio d_j/d_i varies by about 10% as we change the coupling J between the two monomer units, which we cannot tightly constrain without dynamics. We discuss this uncertainty in [Supporting Information, Section S1](#). With both sources of error, we can constrain d_j/d_i to lie in the range [1.6, 2.0]. Our simulations show that $X_{\text{GSB,SE/ESA}}$ qualitatively follows d_j/d_i , indicating that we have identified the quantity on which X reports.

It is important to note that the ratio X is affected by chirp, and therefore we include the experimentally measured group-delay dispersion in our simulations. Otherwise, there would be no way to disentangle the contributions of chirp from the contributions of the relative dipole moments. Chirp affects the relative weight of the peaks along the excitation axis for all orders above third. Chirp changes higher-order peak amplitudes because when chirp is present, some transitions are excited before others. The loss of ground-state population and the presence of selected single-excitation populations, when the lagging frequencies arrive, change the strength of excitation at those lagging frequencies. The impact of chirp on 2DES has been explored previously.^{43–45}

A similar analysis of X could in principle be performed on the peak ratios of the seventh-order signal, as compared with the fifth order. Such an analysis would attempt to quantify the dipole strength connecting double-excited states to triple-excited states. By analyzing successively higher orders, one can in principle build up quantitative information about the dipole ladder of the system. However, the analysis of higher-order signals becomes increasingly challenging with increasing order because each signal contains not only new pathways including highly excited states, but also contributions from all pathways already present in the lower-order signals.²⁸ Therefore, as a consequence of the reduced signal-to-noise ratio of the extracted seventh- and ninth-order signals, we did not perform

this extended analysis. For measurements with a better signal-to-noise ratio, this analysis might be possible.

The experimental $S^{(5)}$ 1Q line shapes are slightly different from the $S^{(3)}$ 1Q line shapes. In particular, the $S^{(3)}$ peaks at $\hbar\omega_\tau = 1.76$ eV shift to $\hbar\omega_\tau = 1.74$ eV in $S^{(5)}$. The simulations in [Figure 3](#) do not fully account for the peak shift and we are uncertain of its cause. The separated orders can be used to measure exciton–exciton annihilation dynamics as a signature of exciton transport. We have shown previously, using TA, that the rise of the fifth-order signal with population time can be used to quantify exciton transport because for annihilation to occur, the excitons first must propagate to get into close spatial proximity.³¹ In addition, the dynamics of the seventh and higher orders can reveal information on the annihilation probability. While in earlier work,³³ we used only the frequency-integrated time evolution, more details about the microscopic processes of exciton–exciton interaction are expected to be found in the higher orders of the 2D line shapes. In the present example of the dimer, the two excitations are essentially colocalized right after excitation. Thus, there is no additional time scale that would represent exciton diffusion, and thus we did not measure it here. However, in general, such observations are useful for more complex samples. [Figure 4](#) shows the contributions to the $S^{(3)}$ and $S^{(5)}$ signals from the various Liouville pathways. The $\text{NSE}^{(5)}$, $\text{NESA}^{(5)}$, $\text{SE}_2^{(5)}$, and $\text{ESA}_2^{(5)}$ pathways of $S^{(5)}$ show a new spectral peak at $\hbar\omega_\tau = 1.72$ eV corresponding to the energy difference between the $|lj\rangle$ biexciton and the $|l\rangle$ exciton energy. This additional peak causes a small but noticeable shift in the ω_τ line shape of the $|l\rangle$ doublet, which is visible by comparing to the $S^{(3)}$ line shapes. However, in the full simulations of [Figure 3](#), the shift in line shape is not as strong and originates from finite-pulse and reweighting effects, because after EEA and relaxation to the $|l\rangle$ exciton, these new peaks exactly cancel between the $\text{NSE}^{(5)}$ and $\text{NESA}^{(5)}$ pathways and the $\text{SE}_2^{(5)}$ and $\text{ESA}_2^{(5)}$ pathways. If there were still a biexciton population, the cancellation would not be complete, and a dynamic peak shift might be observed as a function of population time. Note that this new peak does not appear in the $\text{A}^{(5)}$ pathways, but $\text{A}^{(5)}$ shows a more subtle change in line shape, which is due to the reweighting of pathways, which is central to our analysis of the ratio X above.

In the present work, we have experimentally shown the extraction of nonlinear orders in two-dimensional electronic spectra up to the $S^{(9)}$ signal. The separation of orders was achieved for one-quantum and two-quantum excitation positions through systematic intensity variation. Experiments were carried out on the squaraine dimer dSQBC. The extraction of the various orders revealed differences in the line shapes for the higher-order signals. Most significantly, we observed a shift of the 1Q peak position from the $S^{(3)}$ to the $S^{(5)}$ signals along the $\hbar\omega_\tau$ axis. Furthermore, a direct comparison of the $S^{(5)}$ signal at the 1Q and 2Q positions revealed significant differences in the line shape of the same-order signals: While the signal at the 1Q position consists of two peaks along $\hbar\omega_\tau$, the 2Q signal only shows one broad peak.

All nonlinear order contributions were reproduced with simulations showing quantitative agreement. The separated $S^{(3)}$ and $S^{(5)}$ signals allowed us to quantify the strength of the dipole couplings to the doubly excited states. To gain information on the dipole transition strength, we compared the ratios of the integrated peak intensities of the $S^{(3)}$ and $S^{(5)}$

signals. Through the change in peak intensity we could match the simulation to the experiment and therefore describe the higher-excited states of our investigated sample. Our simulations also showed that the ratio of the pump-weighted average dipole strength of the two singly excited states qualitatively follows the ratio between SE and ESA signals ($X_{\text{GSB,SE/ESA}}$) proving that investigating X presents one way to analyze the dipole strengths of the higher-excited state. This analysis of the dipole strength of higher-excited states was made possible by the order separation.

Furthermore, the simulations allowed us to split the signals into their underlying contributions, which we described using double-sided Feynman diagrams. Through the analysis of the differences between the lower- and higher-order signals, we extracted information about line-shape changes caused by the interaction with the highly excited states. We inferred that the ESA_2 and SE_2 contributions only visible in the higher-order signal include interactions with the higher-excited states. In these signals, an energetic shift is visible, which provides insight into the energetic structure of the highly excited states.

In conclusion, the systematic extraction of several perturbative terms of artifact-free nonlinear-order signals in 2D electronic spectroscopy and the simulations using UFSS provide a unique spectroscopic framework to derive system properties, such as the energetic structure, coupling between states and transition dipole moments, also for higher-excited states. The quantitative agreement needed for this analysis is only achievable through the separation of orders and the removal of higher-order artifacts.

EXPERIMENTAL SECTION

The details of the experimental setup have been discussed elsewhere,^{33,36,46} and here we briefly review the main features. All measurements were performed using an Yb laser (Pharos, Light Conversion) as a light source. The pulses provided have a temporal length of around 0.5 ps and a central wavelength of 1030 nm at a repetition rate of 50 kHz. The pulses were spectrally broadened using an optical parametric chirped-pulse amplifier (Orpheus, Light Conversion) and then separated into pump and probe by a beam splitter (178892, Layertech GmbH), with 90% of the intensity split into the pump beam and the remaining 10% split into the probe beam. The probe beam was delayed by a motorized linear delay stage (M-IMS1000LM-S, Newport) to measure specific population times. Both pulses were compressed by individual prism compressors. The pump pulse was additionally compressed by an acousto-optic modulator (AOM) pulse shaper (Quickshape, Phasatech) at 50 kHz repetition rate. The pulse shaper was also used to provide double pulses with variable delay and intensity. After compression, the probe pulse had a duration of 25 fs (full width at half-maximum of the intensity) and the pump pulse of 14 fs. The pump and probe duration were measured using frequency-resolved optical gating.⁴⁷ Both beams were focused in the sample position, and the beam diameters were determined by fitting a beam-profile measurement with a CMOS camera (acA1280–60gm, Basler) with a Gaussian. The width parameters of this Gaussian fit, corresponding to the diameters at e^{-1} of the maximum amplitude of the beam, show values of $d_x = 86 \mu\text{m}$ and $d_y = 76 \mu\text{m}$ for the probe and $d_x = 134 \mu\text{m}$ and $d_y = 344 \mu\text{m}$ for the pump were obtained. The relative polarization between the pump and probe pulses was set to the magic angle of 54.7° .

The dSQBC sample was dissolved in toluene and the concentration was chosen so that the absorption peak at 1.77 eV showed an optical density of approximately 0.3 OD for a sample thickness of 1 mm.

As described above, we determined the optimal intensities for the separation of the nonlinear orders by first analyzing the population time dynamics in a TA measurement. Then, the saturation behavior of the TA signal was determined at a single population time. Afterward, the noise level of the 2D measurement was identified. From the saturation behavior and noise level, the relative error was calculated, which was used to determine the optimal intensities for separating the nonlinear orders in the 2D measurement. Figure 2 and the corresponding text describe the measurements in more detail.

To separate the four nonlinear orders, we measured four 2D maps at the intensities corresponding to pump pulse energies of 1.74 nJ, 7.35 nJ, 12.9 nJ, and 15 nJ. The pump pulse energies for the power-dependent TA experiment and the 2D experiments were measured with a radiometric photodiode power sensor (PD300-BB-50mW, Ophir Spiricon). For the 2D experiments the pump pulse energies were measured for a single pump pulse. For each 2D map, 251 steps were measured for coherence time τ with a step size of 0.44 fs. The delay steps, the different pump intensities, and the chopping of every second laser shot were performed on a shot-to-shot basis by the AOM pulse shaper. To collect the data, the pump beam was blocked for every second shot and the probe spectrum was detected with a spectrometer (Acton 2156, Princeton Instruments) and a line camera (HS-Kamera Serie3030, Entwicklungsbüro Stresing). The probe spectrum with the pump present was then divided by the probe spectrum in the next shot with the pump blocked. After this division, the logarithm was taken and in the last step the ΔOD values were averaged over all measurements acquired at the same τ and intensity step. Afterward, the data was mirrored along the τ axis around $\tau = 0$ fs with the exception of the $\tau = 0$ fs data point itself, so that the correct 0Q signal was displayed after Fourier transform. The data were then Fourier transformed along τ , and eq 4 was used as described above to extract the nonlinear signal contributions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.6c01715>.

Simulation parameters, Early time dynamics of dSQBC, Saturation behavior of dSQBC, Raw data, Self-consistency checks of extracted orders, Constraining the simulation parameters, Cancellation of $\text{ESA}_2^{(s)}$ and $\text{SE}_2^{(s)}$ pathways by $\text{NESA}^{(s)}$ and $\text{NSE}^{(s)}$ pathways, Concentration-dependent linear absorption spectra, Detection-energy dependence of the extraction error, Effect of chirped pulses on simulation results and Effect of $|j\rangle$ exciton relaxation dynamics on the X ratio. The data that support the findings of this study are openly available in Zenodo at [10.5281/zenodo.21389935](https://doi.org/10.5281/zenodo.21389935) (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ISSUE PUBLICATION

Due to a production error, this paper was published in an issue on August 20, 2026, without all the corrections made. The corrected version was reposted on September 3, 2026.