

# Laser-Limited Signatures of Quantum Coherence

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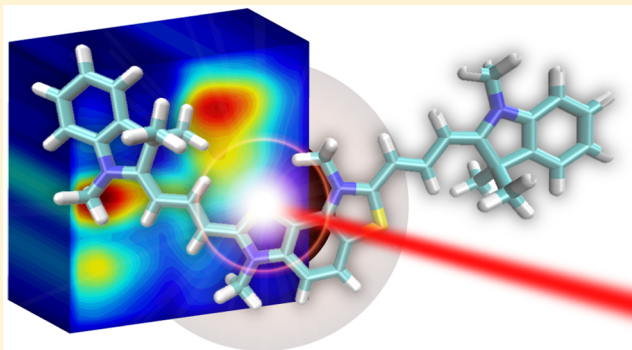
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## S Supporting Information

**ABSTRACT:** Quantum coherence is proclaimed to promote efficient energy collection by light-harvesting complexes and prototype organic photovoltaics. However, supporting spectroscopic studies are hindered by the problem of distinguishing between the excited state and ground state origin of coherent spectral transients. Coherence amplitude maps, which systematically represent quantum beats observable in two-dimensional (2D) spectroscopy, are currently the prevalent tool for making this distinction. In this article, we present coherence amplitude maps of a molecular dimer, which have become significantly distorted as a result of the finite laser bandwidth used to record the 2D spectra. We argue that under standard spectroscopic conditions similar distortions are to be expected for compounds absorbing over a spectral range similar to, or exceeding, that of the dimer. These include virtually all photovoltaic polymers and certain photosynthetic complexes. With the distortion of coherence amplitude maps, alternative ways to identify quantum coherence are called for. Here, we use numerical simulations that reproduce the essential photophysics of the dimer to unambiguously determine the excited state origin of prominent quantum beats observed in the 2D spectral measurements. This approach is proposed as a dependable method for coherence identification.



## INTRODUCTION

Organic molecular aggregates attract considerable interest as potential substitutes for silicon-based photovoltaic cells. Certain proposed implementations are inspired by natural photosynthesis, where photon energy absorbed by the involved pigments is found to traverse through coupled chromophore systems with remarkable efficiency.<sup>1</sup> Recently, quantum beats observed in two-dimensional (2D) spectroscopy of such systems were attributed to robust coherence between electronic states, implying that excitation mobility relies on wavelike motion to minimize losses.<sup>2–4</sup> Interestingly, similar signs of coherent energy transfer were recorded in conjugated polymers,<sup>5</sup> indicating that such quantum effects can potentially be employed as a design principle in synthetic molecules. In fact, recent experimental studies suggested that coherence helps to overcome the electron–hole binding at heterojunctions in organic photovoltaics.<sup>6,7</sup>

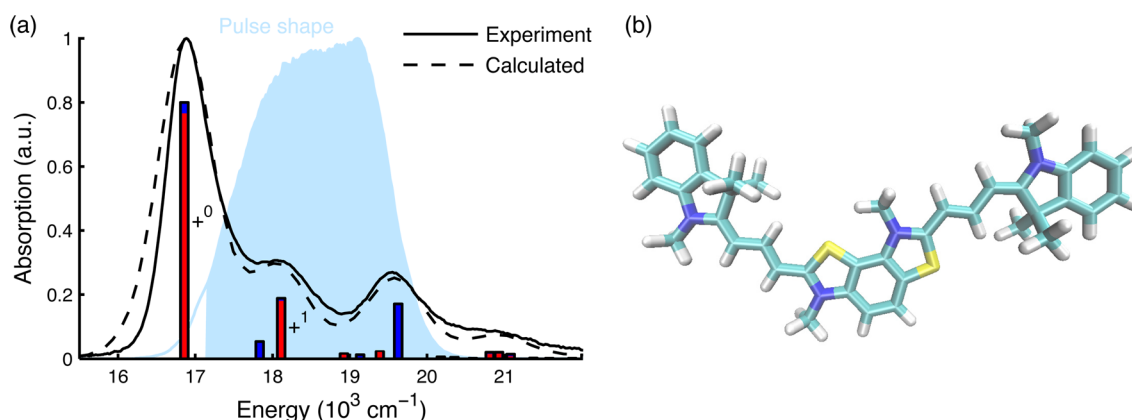
Nevertheless, besides electronically excited states, coherence can also exist in the ground state manifold. For that reason, ground state wavepackets in the form of vibrational excitations can give rise to very similar quantum beats,<sup>8–12</sup> despite having no impact on electronic energy transfer. Therefore, to address

the claims of robust electronic coherence, the recent years have seen a tremendous effort aimed at distinguishing electronic excited state beatings from ground state beatings in ultrafast spectroscopy. Some of the proposed distinction methods rely on the use of laser polarization sequences and two-color excitation pulses;<sup>13,14</sup> however, such approaches call for energetically well-separated excited states and impose experimental complications. Perhaps for that reason, most studies have instead focused on protocols for isolating electronic coherences within the patterns of peak oscillations measured in conventional 2D spectra, where all pulses are identical and share a common polarization.<sup>9,15–21</sup> Notably, Butkus et al. proposed a scheme based on coherence amplitude maps,<sup>18,20</sup> which recently was successfully applied to identify excited state coherences in the Photosystem II reaction center.<sup>21</sup>

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**Figure 1.** Excited states contributing to linear absorption of the cyanine dimer. (a) Experimental (solid curve) and calculated (dashed curve) absorption spectrum. Also shown is a stick spectrum indicating the transitions contributing to the absorption band. For each stick, the red (blue) color represents the contribution of symmetric (antisymmetric) electronic wave functions to the corresponding excited state. The two strongest absorbing excitons with predominant symmetric character are labeled  $+^0$  and  $+^1$ . The laser spectrum used to record the experimental two-dimensional spectra is indicated with the light blue curve, whereas the numerically incorporated laser profile is represented with the solid area (see the [Supporting Information](#) for details). (b) Molecular structure of the dimer, with N and S atoms depicted as blue and yellow, respectively.

In this article, we present room-temperature experimental coherence amplitude maps of a synthetic dimer that cannot be reconciled with the distinctive maps proposed in the literature.<sup>18,20,21</sup> Through accompanying calculations, we demonstrate that the anomalous beating patterns can be understood on the basis of the limited laser bandwidth used in the experiment, which distorts the coherence amplitude maps through a redistribution of oscillation intensities and a shift of spectral peaks. We expect such distortions to be particularly detrimental for light-harvesting systems tuned to absorb over a broad spectral range,<sup>3,22</sup> and in general for the wide variety of synthetic molecules that make up today's prototype photovoltaic and functional optoelectronic materials.<sup>5,7</sup> Because the experimentally recorded beating maps can no longer guide toward the origin of the measured coherence on the basis of the aforementioned distinction criteria,<sup>18,20</sup> we have successfully reproduced the 2D measurements through simulations including the pulse shape, to determine the excited state nature of the observed oscillations on the basis of the numerical data. We propose this procedure as being the most reliable method for the assignment of spectral beatings.

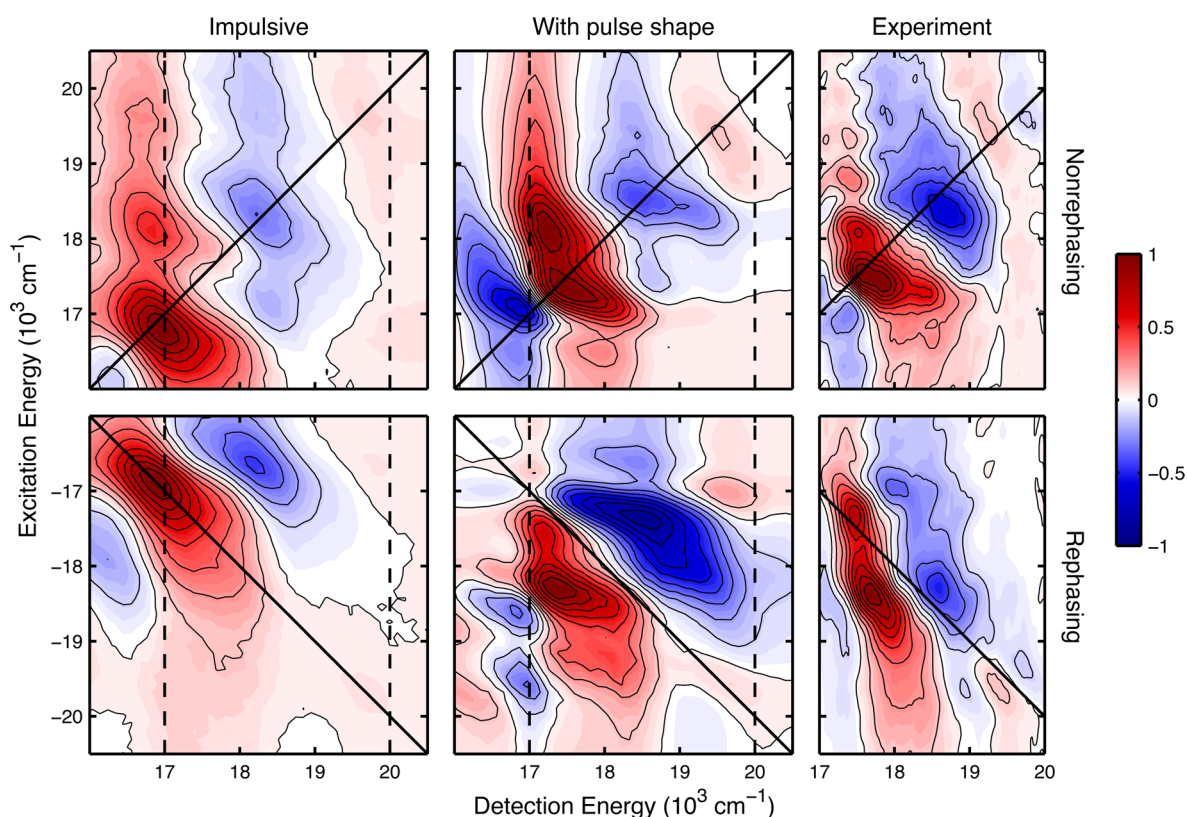
## RESULTS AND DISCUSSION

Recently, several 2D spectroscopic studies have focused on dimers,<sup>11,23,24</sup> the simplest molecules that can host electronic coherence among coupled chromophores. In doing so, one can study the fundamental aspects of quantum coherence without having to interpret an optical response representing a large number of degrees of freedom, as is commonly the case for polymeric systems and pigment–protein complexes.<sup>12</sup> Here, we follow this approach by considering a dimer of two identical cyanine dyes fused together via a common benzene ring; see [Figure 1b](#). Such an arrangement provides a rigid conformation of the two molecular dipoles that acts to maintain a fixed coupling between monomeric subunits and avoids the potential attribution of electronic dephasing to effects linked to sample heterogeneity. Full conjugation through the polymethine structure is prohibited by the monomeric dyes being linked via the *meta*-positions of the central ring,<sup>25,26</sup> allowing us to model this system as two independent interacting dipoles. To further substantiate this, we have performed *ab initio*

calculations ([Supporting Information](#)), demonstrating an antisymmetric and a symmetric state (with respect to mirroring through the benzene ring) at approximately 17 000  $\text{cm}^{-1}$  and 19 500  $\text{cm}^{-1}$ , respectively. This is consistent with the compound being a dimer whose local excitations are of Frenkel-type and interacting through an excitonic coupling of roughly 1250  $\text{cm}^{-1}$  (ref 26).

The linear absorption spectrum of the monomer dye (shown in the [Supporting Information](#)) features a distinct vibronic progression due to coupling of the electronic transition to an intramolecular vibrational mode with a frequency corresponding to 1250  $\text{cm}^{-1}$ . In dimerized form, the combination of vibronic coupling and excitonic interactions results in a complex absorption band containing multiple peaks. Both the monomer and dimer spectra are accurately reproduced using the Holstein Hamiltonian, which includes vibronic couplings explicitly in the quantum Hamiltonian (see the [Supporting Information](#) for details). In doing so, the same parameters are applied for the monomer and dimer, namely a vibrational frequency of 1250  $\text{cm}^{-1}$  and a Huang–Rhys factor (quantifying the coupling strength between the vibrational mode and the electronic transitions within the cyanines) of 0.47. For the dimer, the best agreement was found using an excitonic coupling strength of 1160  $\text{cm}^{-1}$  and an interchromophore twist angle of 129°, both of which are in concord with *ab initio* estimates (see [Supporting Information](#) and ref 26). Also depicted in [Figure 1a](#) is the calculated dimeric stick spectrum, representing the excited states that comprise the absorption profile. For each stick, the red (blue) color indicates the relative contribution of fully symmetric (antisymmetric) electronic wave functions with respect to interchange of the site excitations (note that such a symmetric wave function is antisymmetric upon mirroring and vice versa, due to the obtuse angle between the cyanine moieties). From this, it follows that the two strongest absorbing excitons correspond to the symmetrically enhanced transitions toward the zero- and one-phonon band. For future reference these states are labeled  $+^0$  and  $+^1$ , respectively.

In a 2D spectroscopic experiment,<sup>27,28</sup> a molecular sample interacts with three femtosecond laser pulses after which the molecular response is amplified by a fourth “local oscillator” pulse followed by detection through a spectrometer. The



**Figure 2.** Two-dimensional spectroscopy of the cyanine dimer. Shown are nonrephasing (top row) and rephasing (bottom row) two-dimensional spectra at 70 fs waiting time. Impulsive calculations (left column) result in well-resolved peaks with locations matching those of the exciton bands observed in linear absorption. Inclusion of realistic laser pulse effects (middle column) leads to a shift of the peaks to match the locations as observed in the experiment (right column). In the calculated spectra, the vertical dashes denote the detection window set by the local oscillator.

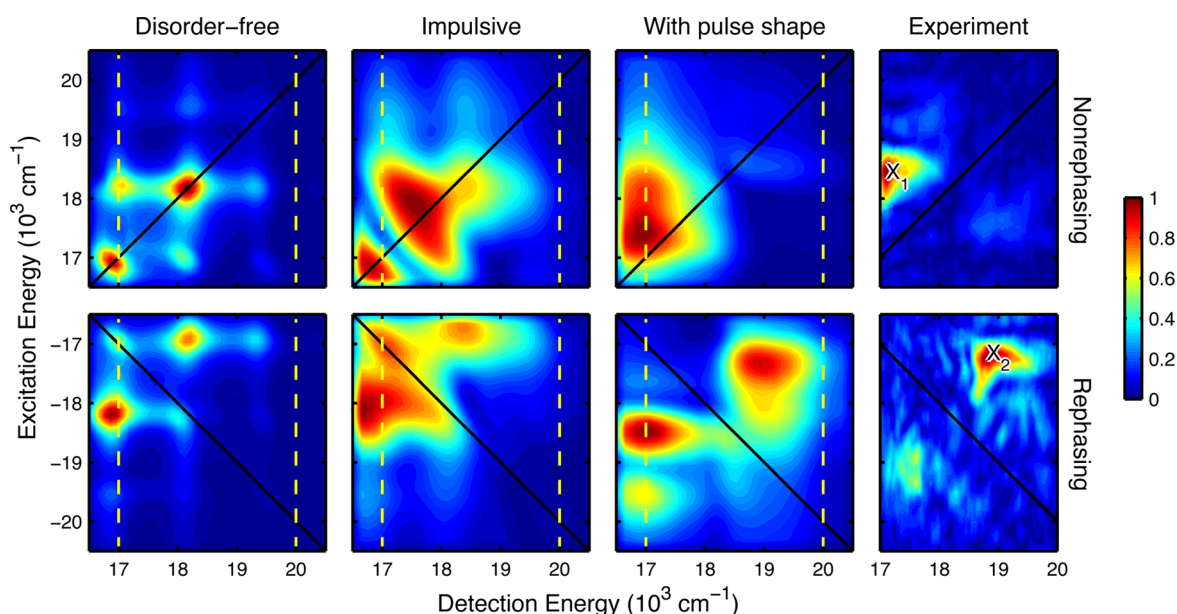
detected signal is conventionally represented as a 2D excitation-detection spectrum for a selected “waiting time”, the time interval between the second and third pulse during which the nonequilibrium superposition of excited states evolves, and can be resolved in a rephasing and nonrephasing contribution. Shown in Figure 2 are representative 2D spectra resulting from measurements and calculations of the dimer. Here, impulsive simulations have been performed by simply taking a 2D Fourier transform of the third-order molecular response function with respect to the excitation and detection time.<sup>27</sup> The resulting spectra feature a dominant emission peak at the diagonal, matching the absorption energy of exciton  $+^0$ . The above-diagonal cross-peak appearing in the nonrephasing spectrum is associated with the  $+^1$  state, likewise matching the expected energy on the basis of the stick spectrum. However, the features in the experimental equivalents appear at spectral locations that are significantly shifted with respect to the impulsively predicted ones. These spectral differences are in line with the anticipated effect of the laser pulse,<sup>29,30</sup> used to record the experimental spectra. Because a significant laser overlap with the  $+^0$  transition was found to result in a predominant contribution of this exciton to 2D spectra (due to the laser selectivity and the fact that peaks in linear absorption roughly come out squared in 2D spectroscopy<sup>27</sup>), the applied pulse was tuned so as to mitigate this transition and enhance the relative contribution of the other excited states. The pulse (shown in Figure 1a) is incorporated numerically by performing a 3-fold convolution of the response function with the optical excitation field<sup>27,29</sup> (see the Supporting Information for details). Through this procedure, the 2D measurements are accurately repro-

duced, indicating that the observed peak shifts are indeed owing to the laser spectrum.

Note that by construct, the pulse sequence used in 2D spectroscopy affects the excitation energy more than the detection energy. The reason for this is that the excitation event involves two interactions with the pulse, whereas detection results from only a single interaction. (Heterodyne detection commonly used to extract 2D spectra allows us to divide out the local oscillator field applied to record the signal.) This explains why in the nonimpulsive simulations, features appear at detection frequencies just outside the pulse spectrum. However, in the experiment the detection energy range is strictly limited by the local oscillator, for which the spectrum is identical to that of the excitation pulses. In the calculations, this windowing effect could be mimicked by truncating the 2D spectra beyond the range depicted by the dashes in Figure 2. Furthermore, a reproduction of the conspicuous absorption features appearing in the rephasing and nonrephasing measurements requires a shift of the two-exciton band by  $750\text{ cm}^{-1}$  in the calculations. A similar shift was found in ref 31 for Frenkel excitations in a lutetium phthalocyanine dimer, which was attributed to electron correlation effects despite the absence of charge transfer states.

An effective way to visualize the pronounced oscillatory behavior seen in the spectral dynamics is by means of coherence amplitude maps, which are obtained through a Fourier transform of the 2D spectra over the waiting time, and which have found numerous applications in experimental studies.<sup>9,15–17,19,21</sup> Furthermore, such maps have recently been shown to help ascertain the origin of spectral beatings. As





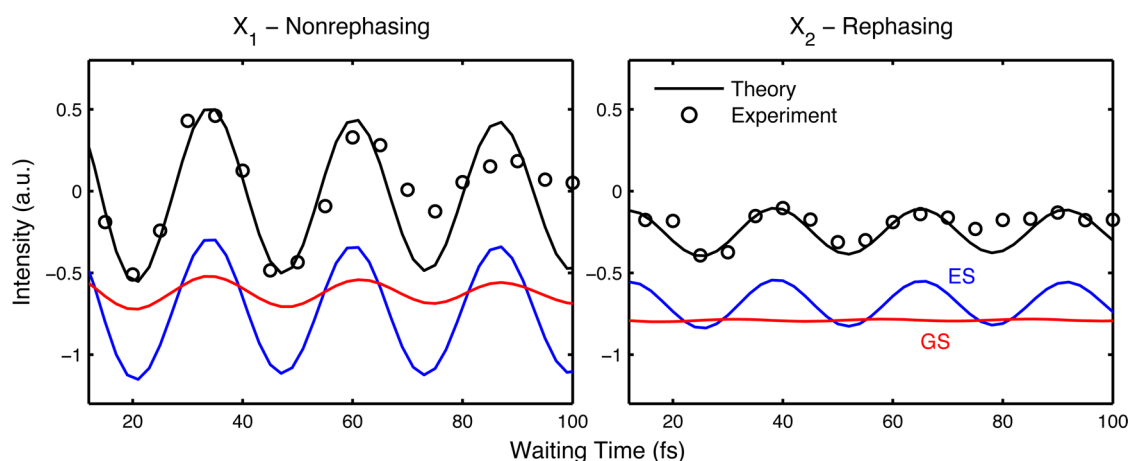
**Figure 3.** Impact of the experimental laser pulse on the spectral dynamics. Nonrephasing (top row) and rephasing (bottom row) coherence amplitude maps at  $1250\text{ cm}^{-1}$ . Shown as a reference are disorder-free impulsive calculations (first column from left), which feature well-resolved peak patterns signifying the origin of the observed coherences. Incorporation of dynamic disorder (second column) broadens the peaks but leaves the patterns intact. Nonimpulsively calculated maps (third column) show a distortion of the peak patterns. This distortion is in accord with the coherent dynamics observed in the experiment (fourth column). Markers  $X_1$  and  $X_2$  indicate the spectral locations from which the traces shown in Figure 4 are extracted.

mentioned earlier, beatings can arise due to vibrational coherences in the electronic ground state, as well as coherences in the electronic excited state. For the latter case, a coherence can take up a predominant electronic character, or a mixed electronic-vibrational (vibronic) character.<sup>32</sup> In ref 20, distinction criteria for these types of coherences were presented for vibronic homodimers with varying coupling strengths following the conformation of Fourier amplitude peaks in the rephasing signal, which was based on calculations under the condition of impulsive excitation. Diagonally symmetric peaks were found to be indicative of electronic coherence whereas strong oscillations at the diagonal represent a predominant vibrational character.<sup>20</sup> Furthermore, deviations from the spectral diagonal and its parallels, offset by multiples of the vibrational quantum, represent vibronic coherence.<sup>21</sup>

The coherence amplitude maps measured for the dimer are shown in Figure 3 for a beating frequency of  $1250\text{ cm}^{-1}$ . These maps capture the most significant dynamics, as this energy matches both the vibrational quantum and the splitting between the most prominent excitons (recalling the stick spectrum in Figure 1a). Also shown are maps calculated under different simulation conditions. Impulsive calculations without energy fluctuations due to the solvent environment (disorder-free) result in well-resolved Fourier patterns bearing strong similarity with those found for a strongly coupled dimer in ref 20. Additional impulsive simulations including disorder show only a broadening of the beating peaks, leaving the peak conformation found in the disorder-free case intact. However, coherence amplitude maps derived from the experimental 2D spectra are surprisingly different. In contrast to the impulsively calculated maps, which are rich in features, they show spectral dynamics concentrated in only a few distinct Fourier peaks. This indicates that the pulse shape effect on such maps is more dramatic than the peak shifts observed for the 2D spectra. The influence of the limited spectral width of the laser is further

elucidated by comparative nonimpulsive calculations, showing a significant relocation of the beating features in the excitation-detection spectrum, and a drastic redistribution of oscillation intensities. The experimental Fourier peaks can be well understood on the basis of the trend observed in the calculations upon inclusion of the pulse shape, especially when considering that peaks lying outside the local oscillator range (indicated with dashes) are expected to be highly suppressed in the measurements. Furthermore, the low-energy diagonal peak appearing in the calculated nonrephasing signal is likely susceptible to the laser spectrum which only partly covers the associated optical transition, considering that this feature experiences three weightings with the pulse shape. In that respect, particularly the rephasing maps show excellent agreement.

From our comparison between experiment and theory, it follows that the distortions observed in the measured coherence amplitude maps derive from the limited spectral width of the laser compared to the molecular absorption band. We anticipate that such distortions are not unique to the dimer under consideration, but that compounds with similar absorption bandwidths are equally susceptible to the laser pulse. More generally, considering that the laser pulse duration applied in our study is typical for current 2D electronic spectroscopic experiments, we expect such distortions to occur for experiments on molecules whose bands are similar to or exceeding the cyanine dimer. As follows from Figure 1, the dimer absorption ranges over roughly  $3500\text{ cm}^{-1}$  (measuring the width of the band with at least 20% of the maximum intensity; this approximate measure is consistently applied for numbers quoted in the following). This width is typical for polymers that form prototype candidates for organic optoelectronic devices. For example, P3HT absorbs over a range of  $5500\text{ cm}^{-1}$  (ref 33) whereas MEH-PPV has a  $7000\text{ cm}^{-1}$  bandwidth.<sup>5</sup> Both these polymers displayed quantum beats in



**Figure 4.** Excited state coherences probed under realistic excitation conditions. Shown are measured (markers) and calculated (black curves) spectral traces taken at location  $X_1$  (left) and  $X_2$  (right) in nonrephasing and rephasing spectra, respectively (Figure 3). In both cases, the simulated periodicity matches the experimental measurements. Furthermore, a dissection of the calculated traces into (electronic) excited state (ES, blue curves) and ground state (GS, red curves) contributions reveals a predominant excited state origin of the observed coherences.

ultrafast spectral measurements.<sup>5–7</sup> Furthermore, a comparably broad absorption band is also found for certain light-harvesting complexes where coherence is said to play a central role in mediating exciton dynamics. Notable examples are the proteins PC645 and PE545, both found in certain species of marine algae, having widths of 4000 and 3500  $\text{cm}^{-1}$ , respectively.<sup>3</sup> Besides, we expect pulse-induced distortions to occur when carotenoids are in play,<sup>22,34,35</sup> which typically absorb over 6000  $\text{cm}^{-1}$ .

With the distortion of characteristic beating patterns in the experiment, the aforementioned distinction criteria based on coherence amplitude maps become inapplicable. As shown in Figure 3, accompanying calculations capturing the essential molecular photophysics could help to reconstruct the coherence amplitude maps to unravel the origin of observed quantum beats. However, once such calculations are at hand, this origin can be determined readily through an analysis of the different contributing Liouville pathways. For the dimer under consideration, it is particularly interesting to investigate whether the beatings observed in the experiment are of electronically excited state origin, and whether the associated dephasing times can be extracted from them. To address this, a Liouville pathway analysis has been carried out in Figure 4, for the spectral locations where oscillatory transients are present in the measurements (labeled  $X_1$  and  $X_2$  in Figure 3). A dissection of the total time-dependent signal amplitude into excited state and ground state contributions demonstrates that excited state coherences are predominantly responsible for the observed beatings. Furthermore, the good agreement between calculated and measured spectral traces, and the clean single-component oscillation (with a frequency corresponding to 1250  $\text{cm}^{-1}$ ) observed in both cases supports an unambiguous measurement of the associated coherence time.

The coherence time following from the calculated spectra is well beyond the expected onset of electronic dephasing, confirming that coupling of electronic transitions to intramolecular vibrational modes can prolong the associated coherences.<sup>11,36,37</sup> Complementary calculations demonstrate that the observed beatings are predominantly due to the strongest absorbing excitons  $+^0$  and  $+^1$  (Supporting Information). These excitons are electronically similar (that is, symmetric), while differing mainly in the number of involved

vibrational quanta (in the electronically excited potential). As a result, the associated exciton energies perform correlated fluctuations under the influence of dynamic disorder in the environment such that quantum phase is conserved for longer times.<sup>11,36</sup> However, the experimental beatings are found to decay significantly faster, that is, on the typical time scale for electronic dephasing.<sup>11</sup> A possible explanation for such a short coherence is a rapid dephasing mechanism being in effect for the vibrational modes in the experiment, resulting in a loss of correlation between the fluctuating exciton energies. A similar excited state coherence time was found in experiments on a different cyanine dimer,<sup>11</sup> suggesting this vibrational dephasing to be common to cyanine-based aggregates. As expected from the numerical results, a suppression of this dephasing mechanism would significantly enhance the robustness of excited state quantum effects.

Whereas for 2D spectroscopy there is an inevitable congestion of ground state and excited state coherent transients, a recent theoretical study proposed time-resolved fluorescence as a technique to detect coherent excited state dynamics without contributions from the ground state manifold.<sup>38</sup> This theory just found its first implementation in an experimental study on perylene bisimides.<sup>39</sup> The advantage of exclusively probing processes in the excited state manifold is at the cost of an inferior time resolution as compared to 2D spectroscopy, although gradual progress is being made. We therefore anticipate that for the time being, 2D spectroscopy remains unbeaten as a probe for coherent dynamics.

## CONCLUSION

The currently accepted method for distinguishing coherent superpositions of electronic excited states from ground state vibrational wavepackets relies on coherence amplitude maps, which consist of the Fourier pattern of quantum beats observed in 2D spectroscopy. Criteria for subsequent coherence identification based on these maps have been derived under the conditions of impulsive optical fields. In this article, we have presented experimental coherence amplitude maps of a cyanine dimer, for which pulse induced distortions render the identification criteria inapplicable. We argue that similar distortions are to be expected for the prototypes of organic photovoltaics, as well as for certain light-harvesting complexes,

and that other ways of identifying quantum coherence are called for. We resolve this by using spectral simulations accounting for the laser pulse envelope to capture the essential photophysics of the dimer, thus unambiguously determining the excited state origin of observed quantum beats. We propose this approach as a dependable alternative for coherence identification, offering a controlled methodology toward understanding how exciton coherences may be harnessed for future light-harvesting applications.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b10312.

Supplementary data from time-dependent density functional theory (TDDFT), experiments, and spectral modeling. We additionally provide a detailed description of the synthesis of the monomer and dimer compounds, spectroscopic experiments, and TDDFT and spectral modeling procedures. Full refs 6 and 31 can also be found here. (PDF)

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### Notes

The authors declare no competing financial interest.

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