In Silico Ultrafast Nonlinear Spectroscopy Meets Experiments: The Case of Perylene Bisimide Dye

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ABSTRACT: Spectroscopy simulations are of paramount importance for the interpretation of experimental electronic spectra, the disentangling of overlapping spectral features, and the tracing of the microscopic origin of the observed signals. Linear and nonlinear simulations are based on the results drawn from electronic structure calculations that provide the necessary parameterization of the molecular systems probed by light. Here, we investigate the applicability of excited-state properties obtained from linear-response time-dependent density functional theory (TDDFT) in the description of nonlinear spectra by employing the pseudowavefunction approach and compare them with benchmarks from highly accurate RASSCF/RASPT2 calculations and with high temporal resolution experimental results. As a test case, we consider the prediction of femtosecond transient absorption and two-dimensional electronic spectroscopy of a perylene bisimide dye in solution. We find that experimental signals are well reproduced by both theoretical approaches, showing that the computationally cheaper TDDFT can be a suitable option for the simulation of nonlinear spectroscopy of molecular systems that are too large to be treated with higher-level RASSCF/RASPT2 methods.

1. INTRODUCTION

Nonlinear electronic spectroscopy with temporal resolution down to the femtosecond (fs) time scale has become an increasingly important tool for studying the structure and dynamics of molecular systems, ranging from single molecules to large molecular aggregates.1−5 In typical nonlinear spectroscopy experiments, a sequence of laser pulses, with controlled time delays and phases, is focused on the sample to bring it out of equilibrium and subsequently monitor its evolution. Specifically, in transient absorption (TA) and two-dimensional electronic spectroscopy (2DES), two interactions with the pump laser field prepare the system in an initial excited state. The relaxation back to equilibrium is monitored by illuminating the system with a delayed pulse (i.e., the probe) and scanning the pump-probe delay. The molecular dynamics is captured indirectly by means of the spectral dynamics of ground-state bleaching (GSB) of the photoexcited transition, stimulated emission (SE) from the prepared excited state to the ground state, and photoinduced absorption to high-lying states. With respect to TA, 2DES provides resolution not only in the detection but also in the excitation frequency axis, delivering for each value of the pump-probe delay a 2D map correlating the excitation and detection frequencies.

Despite the continuous technical progress in ultrafast spectroscopy, the direct interpretation of the measured transient spectra, often congested by many overlapping contributions of different origins, may be hard and rarely univocal. The integration of experimental and computational approaches has therefore become of paramount importance in the analysis and interpretation of transient optical spectroscopy, spanning the infrared−vis−UV spectral regimes,6−9 enabling the disentanglement of all measured features, and obtaining a detailed and reliable description of the system dynamics.

The reliability of simulations to support the interpretation of experimental signals and furnish a microscopic understanding of the studied molecular systems is grounded on an accurate description of the molecular electronic structure and a simple and robust model for the spectroscopic technique, able to provide connection with the experimentally measured observables.10 Accurate electronic structure calculations can be obtained from a wide range of methodologies, some of which are readily available in standard quantum chemistry (QC) packages. In theoretical nonlinear spectroscopy studies, the
electronic structure is usually obtained from multireference methods, such as the restricted active space self-consistent-field (RASSCF) and its second-order perturbation theory variant (RASPT2) due to their universal and potentially accurate treatment of highly excited states required for simulating TA/2DES features. Indeed, a well-designed active space can describe simultaneously and on an equal footing states of different characters, such as covalent and ionic (e.g., charge transfer), and single and multiple excitations. For instance, the RASSCF/RASPT2 level of theory has been utilized recently to simulate fully ab initio TA spectra of the ultrafast nonadiabatic dynamics of several organic molecules—azobenzene, pyrene, uridine and thymidine, and thiouracil—in remarkable agreement with the experiment.

The high computational cost of multireference methods limits their applicability to relatively small active spaces. An inexpensive alternative for the treatment of molecular systems is the linear-response formulation of time-dependent density functional theory (TDDFT). Although in its original formulation TDDFT describes only excitations from the ground state, and it is thus unsuitable to the description of nonlinear spectroscopy, it can be a valuable tool in cases where the initial excited state is predominantly single determinant. In this case, an initially excited state can be prepared enforcing the singly excited configuration with the maximum-overlap method and then can be used as a reference for the TDDFT computation, eventually yielding the desired TA features.

In this work, we explore the applicability of excited states obtained from TDDFT in the description of a nonlinear optical response by employing the pseudowavefunction approach and provide benchmarks against the highly accurate RASSCF/RASPT2 method. Both computational approaches are compared to the experimental results obtained by high time-resolution TA and 2DES spectroscopy on the bis-cationic PBI-(R+)2 (R+ being the 2-(trimethylammonium)ethylene carboxylic acid bisimide dye, hereafter labeled perylene bisimide) and outlines possible routes for further developments.

The concluding paragraph summarizes the presented material and outlines possible routes for further developments.

2. THEORETICAL METHODS
We first show how QC ingredients enter in the simulation of spectroscopy, highlighting the electronic structure calculations that need to be performed to access the molecular manifold of states. We introduce the extended linear-response TDDFT approach, capable of providing dipole moments and excited-state dipole couplings. RASSCF/RASPT2 computations are then presented. Test calculations were performed on both the neutral PBI and the PBI-(R+)2 dication, whose molecular structures are shown in Figure 1. PBI-(R+)2 is the system synthesized and investigated experimentally. The neutral PBI, characterized by a higher symmetry with respect to the cationic species (C2v and C2h, respectively) is computationally more tractable, especially for energy-gradient calculations. Since the electronic structure of both molecules is nearly identical (as discussed in Sections S3—S5 of the Supporting Information), QC calculations and spectral simulations at both the RASSCF/RASPT2 and TDDFT levels of theory were performed on the neutral PBI.

2.1. Spectroscopy Simulations Including Harmonic Vibrations. The response function formalism is the natural framework in which analytic expressions for the description of linear and nonlinear spectroscopy can be written, also including harmonic vibrations (via cumulant expansion of Gaussian fluctuations). A detailed presentation of the spectroscopic methods employed herein is shown in ref 10. Concisely, one considers a molecular system described by a time-dependent Hamiltonian

\[ \hat{H}(t) = \hat{H}_0 - \hat{V}(t) \]  
(1)

where \( \hat{H}_0 \) is the field-free molecular Hamiltonian and \( \hat{V} \) is the operator that couples an external laser field of the form \( F(t) \) with the system. Within the electric dipole approximation, valid when the wavelength of the external field is long compared to the molecular dimensions, the field-molecule coupling takes place via the electric dipole operator \( \mu \).

The response of an observable \( \Omega(t) \) to the external field \( F(t) \) is given by

\[
\Omega(t) = \sum \int_0^t dt_0 F(t - t_0) \int_0^\infty dt_1 F(t - t_1 - t_0) ... \times \int_0^\infty dt_n F(t - t_n - ... - t_1) R^{(n)}(t_n, t_{n-1}, ..., t_1)
\]

(2)

where \( R^{(n)}(t_n, t_{n-1}, ..., t_1) \) is the \( n \)th-order response function defined as

![Figure 1](image-url)
The excited-state energy gradients and ground-state normal modes and frequencies are used to construct vibrational spectral densities that eventually encode the intramolecular part of the electronic-nuclear coupling. Coupling between the electronic states and the environment (e.g., the solvent) is induced by a phenomenological overdamped Brownian oscillator (OBO) spectral density, whose functional form is given by

$$J_{\text{OBO}}(\omega) = \frac{2\lambda}{\omega^2 + \Lambda^2}$$

where $\lambda$ is the solute–solvent interaction strength (or, in other words, the solvent-induced reorganization energy) and $\Lambda^{-1}$ is the so-called dephasing (or correlation) time. These two parameters are typically fitted to the experimental data. Here, we employed $\lambda = 240 \text{ cm}^{-1}$ and $\Lambda^{-1} = 40 \text{ fs}$.

All the spectra presented here have been computed employing the sum-over-states approach implemented in the Spectron software package for the simulation of optical spectroscopy.31 The information flow from the QC codes to Spectron, as well as the analysis and plotting of the obtained spectroscopic data, is managed through the recently developed iSPECTRON interface.32 Reference 10 also contains details about Spectron functioning, inputs, and parameters.

### 2.2. Pseudowavefunction Approach to TDDFT.

By considering the response in the density to a density perturbation (the density–density response), one can obtain a hierarchy of nth-order corrections to the density response that can be used in the computation of transition properties. Such an approach, when applied to density functional theory (DFT), yields the well-known equations for linear-response TDDFT, as well as their higher-order analogues.13

TDDFT gives access to a perturbed pseudowavefunction34 that may be employed in the computation of transition moments between the ground and excited states.13,15 However, in order to simulate nonlinear spectroscopy, transition moments between excited states are required as well. These transition moments arise naturally as part of the quadratic response and may be obtained as its double residue. Nonetheless, it has been demonstrated that for approximate theories like TDDFT, the quadratic response contains unphysical poles whenever the transition energy between two excited states matches the excitation energy of any other state.36–38 These unphysical features may be tamed by employing a complex polarization propagator approach at the expense of losing valuable information regarding the nature of the states participating in the absorption process, but the unphysical poles are still present and give rise to resonances that have no equivalent in exact theory. Hence, the quadratic-response formalism has to be used with caution, and furthermore, its additional computational cost imposes limitations on the size of the systems that can be studied.39

An alternative that has been widely employed in the computation of derivative couplings23,34,40 and transition moments between excited states31,42–44 is to completely neglect dynamical orbital relaxation effects and use the amplitudes obtained from linear-response TDDFT to construct excited-state couplings and transition moments including up to single excitations.

In the TDDFT pseudowavefunction formalism,34 an excited-state pair $\{\Phi_S, \Phi_L\}$ is defined as

$$|\Phi_S \rangle \equiv (X^K + \hat{X}^K \hat{Y}^L \{\Phi_S\})$$

where $X$ and $Y$ are electronic and nuclear operators, respectively, $K$ and $L$ are indices for electronic and nuclear configurations, and $\{\Phi_S\}$ is a set of excited states.
Table 1. RASSCF/RASPT2 and TD-DFT Results for the Relevant (Spectroscopically Bright) PBI States: Labels, Symmetry, and Leading Configurations (Weights > 0.05) of the States Involved in the Transitions, as Well as Associated Energies (in eV) and Oscillator Strengths*  

| transition | state symm. | arrival state config. | weight | trans. energy | $f$ |
|------------|-------------|-----------------------|--------|---------------|-----|
| $S_0 \rightarrow S_1$ | $A_g \rightarrow B_{1u}$ | HOMO $\rightarrow$ LUMO | 0.70 | 2.35 | 0.40 |
| $S_1 \rightarrow S_2$ | $B_{1u} \rightarrow A_2$ | HOMO $\rightarrow$ LUMO + 1 | 0.26 | 1.78 | 0.38 |
| $S_1 \rightarrow S_{12}$ | $B_{1u} \rightarrow A_2$ | HOMO $\rightarrow$ LUMO | 0.07 | | |
| | | HOMO $\rightarrow$ LUMO + 1 | 0.22 | 2.16 | 0.14 |
| | | HOMO $\rightarrow$ LUMO | 0.08 | | |
| | | HOMO $\rightarrow$ LUMO + 2 | 0.06 | | |

*Note that the TD-DFT configurations have been referred to the closed-shell configuration to facilitate the comparison with the RASSCF/RASPT2 results. The state order was assigned according to increasing energy (regardless of symmetry). Single and double arrows denote singly and doubly occupied to virtual transitions, respectively. The orbital labeling is consistent in the two sets of computations (see Figure S4 in the Supporting Information).

and

$$\langle L \rangle \equiv \langle \hat{X}^K + \hat{Y}^K | \Phi_{SS} \rangle$$

where $\langle \Phi_{SS} \rangle$ is the reference Kohn–Sham determinant, in which this work is chosen to be a relaxed singly excited reference. The excitation operators take the form

$$\hat{X}^K = \sum_{ia} X_{ia}^K \hat{a}_i \hat{a}_a$$

$$\hat{Y}^K = \sum_{ia} Y_{ia}^K \hat{a}_a \hat{a}_i$$

where the indices $i, j$ and $a, b$ correspond to orbitals that are occupied and virtual in the reference determinant, respectively, and the amplitudes $X_{ia}^K$ and $Y_{ia}^K$ are the solutions of

$$\left( \begin{array}{cc} A & B \\ B^* & A^* \end{array} \right) \left( \begin{array}{c} 1 \\ 0 \end{array} \right) = \alpha_{K} \left( \begin{array}{c} X_{ia}^K \\ Y_{ia}^K \end{array} \right)$$

with

$$A_{ia,ib} = (\epsilon_i - \epsilon_j) \delta_{ib} \delta_{ia} + (\text{ialb}) - c_s (ijlab) + f_{ia,ib}^{xc}$$

$$B_{ia,ib} = (\text{ialb}) - c_s (ijlab) + f_{ia,ib}^{xc}$$

where

$$(pq|rs) = \int dx \int dr \int dx' \int dr' \phi_p^*(x) \phi_q^*(y) \left( \frac{1}{r - r'} \right) \phi_r(y) \phi_s(r)$$

and

$$f_{pq,rs}^{xc} = \int dx \int dr \int dx' \int dr' \phi_p^*(x) \phi_q^*(y) \left( \frac{\delta^2 E_{pq}}{\delta \phi_p \delta \phi_q} \right)_{\phi_r(y)} \phi_r(y) \phi_s(r)$$

where $\epsilon_p$ denotes the Kohn–Sham orbital eigenvalue for the single-particle orbital $\phi_p$, $c_s$ controls the amount of exact exchange, and $E_{xc}$ is the exchange–correlation energy. Indices $p, q, r, s$ denote generic orbital labels.

The transition dipole moment, $\mu_{KL} = \langle K | \mu | L \rangle$, can then be obtained directly as

$$\mu_{KL} = \sum_{ij} (X_{ij}^K Y_{ij}^L - Y_{ij}^K X_{ij}^L) (\delta_{ib} \delta_{ia} - \delta_{ia} \delta_{ib})$$

where the electric dipole operator has the form $\hat{\mu} = -\sum (\phi_j \hat{r} \phi_i^* | \phi_i \hat{r} \phi_j^*)$. Note that the transition moments given by eq 16 correspond to transitions between unrelaxed TD-DFT states and differ from those obtained from the quadratic response by the total neglect of the second-order relaxation of the density matrix.

Here, we demonstrate that this simplified approach yields accurate transition moments that compare well with those obtained from state-of-the-art RASSCF/RASPT2 for several multiphoton spectroscopy simulations.

2.3. Electronic Structure Calculations. Electronic structure calculations at both the RASSCF/RASPT2 and DFT levels were performed on the neutral PBI in the gas phase. As already mentioned, test calculations on PBI-(R+)_2 give an extremely similar manifold of states (see the Supporting Information). This may be ascribed to the fact that the positive charges of the cationic species are localized on the lateral trimethylammonium moieties, that is, outside the photoactive region, which is identical in the two molecules. Simulation of PBI and PBI-(R+)_2 LA is also shown to give comparable spectra (Figure S1 of the Supporting Information). For this reason, the computationally more tractable PBI is studied here.

2.3.1. RASSCF/RASPT2. The PBI geometry was optimized at the MP2/ANO-L-VDZP level by imposing $D_{2h}$ symmetry. Vibrational ground-state frequencies were computed numerically at the same level of theory. The ANO-L-VDZP basis set was also employed in the RASSCF/RASPT2 computations.

For both compounds, an active space consisting of 20 electrons in 20 orbitals was utilized and combined with a RAS protocol including up to quadruple excitations. The final SA-10-RASSCF(20,4,4;10,0,10) active space (where the first three
indices denote the total number of electrons, the upper limit of holes in RAS1, and the upper limit of excitations in RAS3, respectively; while the last three indices denote the number of orbitals included in the three subspaces: in order, RAS1, RAS2, and RAS3) is shown in Figures S2 and S3 of the Supporting Information. The single-state (SS) RASPT2 method (using the imaginary and IPEA shifts set to 0.2 and 0.0 Hartree, respectively) was employed on the SA-RASSCF wavefunction to correct the state energetics, and transition dipole moments were computed with the state-interaction method on the SA-RASSCF-optimized wavefunction. Energy gradients of the relevant (bright) excited electronic states in the Franck–Condon region were computed numerically at the (SS) RASPT2 level of theory (step size set to 0.005 Å).

The lowest 10 electronic states were considered for each of the four irreducible representations of the PBI $D_{4h}$ point group. The full data set is listed in Table S2 of the Supporting Information, whereas energies and oscillator strengths for transitions of interest are listed in Table 1. All the multireference computations were performed with the QC software package OpenMolcas.46,47

2.3.2. TDDFT. All DFT and TDDFT calculations employed the CAM-B3LYP exchange correlation functional and the 6-311G** basis set. The excited-state reference ($S_1$) was created by promoting an electron from the HOMO to the LUMO, by promoting an electron from the HOMO to the LUMO, with 4 fs time steps. For 2DES experiments, a sequence of three pulses which were separated by a delay very close to the pump–probe delay was needed in order to create the 2D excitation/detection maps. The third pulse acted as a probe, and it was delayed with respect to the second pulse by $t_f$ (the so-called population time or waiting time). The nonlinear signal was measured by a spectrometer placed in the probe pulse direction, which provides the resolution of the signal along the detection frequency axis. The acquisition of a single 2DES map at a fixed $t_f$ was obtained by Fourier-transforming the detected signal with respect to $t_f$ for each spectral component of the probe. The result of this procedure was a 2DES map that correlates excitation and detection frequencies. This procedure was repeated for each population time $t_f$. In this way, a sequence of 2DES maps was collected. In our apparatus, 2DES experiments were performed by introducing a birefringent delay line on the pump optical path in order to create two phase locked pulse- replicas, the translating-wedge-based identical pulses encoding system. In this way, the sequence of the two properly delayed pump-pulses was focused on the sample, together with the probe pulse, which was then collected onto the spectrometer. 2DES maps were generated by continuously scanning the coherence time from $-100$ to $250$ fs at a fixed waiting time and by Fourier-transforming the acquired data along the coherence time $t_f$. In this so-called partially collinear pump–probe geometry, the so-called rephasing and non-rephasing signals propagated along the same direction, allowing us to directly detect the 2DES absorptive spectra. We used the same pump fluence as for the TA experiments and we scanned the $t_f$ delay up to $250$ fs with $4$ fs time steps. Frequency analysis of TA data was performed by Fourier-transforming the residual oscillations of the $\Delta T/T$ signal with respect to the waiting time at each individual detection wavelength. All the experiments were performed in a $200$ μm cuvette of a solution of $1$ mM PBI--$R^-(R^+)$ in acetonitrile.

In the simulation of spectra, to better mimic the experimental conditions, where TA and 2DES signals were recorded by employing pulses with a finite duration and bandwidth, the simulated signals (obtained in the limit of delta-like/infinitesimal bandwidth pulses) were filtered along the excitation frequency axis with the experimental pulse frequency–domain profile (see Figure S8 in the Supporting Information) while describing the finite time resolution by convoluting the different $t_f$ spectra with a Gaussian function with standard deviation $\sigma = 6.5$ fs (corresponding to a FWHM of $\sim 15$ fs).

3. EXPERIMENTAL TECHNIQUES

TA and 2DES experiments were performed using a home-built apparatus described in detail elsewhere. Briefly, the setup was pumped by a Ti:Sapphire laser operating at 1 kHz and emitting 100 fs pulses centered at 800 nm. Such pulses were used to pump a noncollinear optical parametric amplifier (NOPA) that generates pulses with a spectrum spanning from $510$ to $700$ nm, compressed down to a sub-20 fs temporal duration by a chirped-mirror pair. For TA experiments, the NOPA output was split into two optical paths where pump and probe pulses were properly delayed. Both the pump and probe were noncollinearly focused on the sample, and the transmitted probe beam was then collected onto a high-speed spectrometer to obtain differential transmission ($\Delta T/T$) maps as a function of the probe wavelength and probe delay. The pump fluence was set to $80$ μJ/cm², and the pump–probe delay was scanned up to $1000$ fs with $4$ fs time steps. For 2DES experiments, a sequence of three delayed pulses was needed in order to create the 2D excitation/detection maps. The first and the second pulses acted as pump pulses which were separated by a delay $t_f$ (so-called coherence time). The third pulse acted as a probe, and it was delayed with respect to the second pulse by $t_f$ (the so-called population time or waiting time). The nonlinear signal was measured by a spectrometer placed in the probe pulse direction, which provides the resolution of the signal along the detection frequency axis. The acquisition of a single 2DES map at a fixed $t_f$ was obtained by Fourier-transforming the detected signal with respect to $t_f$ for each spectral component of the probe. The result of this procedure was a 2DES map that correlates excitation and detection frequencies. This procedure was repeated for each population time $t_f$. In this way, a sequence of 2DES maps was collected. In our apparatus, 2DES experiments were performed by introducing a birefringent delay line on the pump optical path in order to create two phase locked pulse- replicas, the translating-wedge-based identical pulses encoding system. In this way, the sequence of the two properly delayed pump-pulses was focused on the sample, together with the probe pulse, which was then collected onto the spectrometer. 2DES maps were generated by continuously scanning the coherence time from $-100$ to $250$ fs at a fixed waiting time and by Fourier-transforming the acquired data along the coherence time $t_f$. In this so-called partially collinear pump–probe geometry, the so-called rephasing and non-rephasing signals propagated along the same direction, allowing us to directly detect the 2DES absorptive spectra. We used the same pump fluence as for the TA experiments and we scanned the $t_f$ delay up to $250$ fs with $4$ fs time steps. Frequency analysis of TA data was performed by Fourier-transforming the residual oscillations of the $\Delta T/T$ signal with respect to the waiting time at each individual detection wavelength. All the experiments were performed in a $200$ μm cuvette of a solution of $1$ mM PBI--$R^-(R^+)$ in acetonitrile.

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4. RESULTS AND DISCUSSION

4.1. Electronic Structure Method Comparison. Minor differences are observed for the optimized ground-state molecular geometries at the MP2/AN0-L-VDZP and DFT–(CAM-B3LYP)/6-311G** levels of theory, with slightly shorter bond lengths (ca. 0.01/0.02 Å) exhibited at the DFT level. A comparison, at the optimized geometries, between RASSCF/RASPT2 and TDDFT for several relevant excited states—state energies, symmetry, main configurations, and oscillator strengths—is presented in Table 1. To facilitate the comparison with the RASSCF/RASPT2 results, configurations at the TDDFT level have been referred to the closed-shell configuration. The original TDDFT results (which instead refer to the HOMO → LUMO configuration) are listed in Table S1 of the Supporting Information.

Both methods describe the first excited state (of $B_{3u}$ symmetry, labeled $S_1$, as dominated by the HOMO → LUMO configuration (weight $> 0.70$) with comparable oscillator strengths. Thereby, TDDFT slightly underestimates the transition energy. Both methods predict two bright transitions out of $S_1$ to higher-lying states ($S_2$ and $S_{12}$ at RASSCF/RASPT2 and $S_1$ and $S_2$ at TDDFT) that are expected to give rise to ESA features. Notably, the involved states exhibit a marked multiconfigurational character, dominated by configurations describing a single-electron transition with respect to...
the HOMO → LUMO configuration of the S₀ state. These one-electron transitions are of three types as follows: (a) from the HOMO to LUMO, conferring a partial double excitation character to the transition; (b) from a doubly occupied orbital to the HOMO; and (c) from the LUMO to an empty virtual orbital (see Table S1). We note that the double HOMO ⇒ LUMO arrival state configuration could not be captured by standard TDDFT using the ground-state wavefunction as a reference, but it arises naturally here because an excited state (in this case S₁) is prepared and used as the reference. The optically bright lowest excited state from S₁ is predicted by both RASSCF/RASPT2 and TDDFT to be of A₁g symmetry (labeled S₇ and S₅ at RAS and TDDFT levels, respectively) and to lie ca. 1.75 eV above S₁. RASSCF/RASPT2 predicts the S₁ → Sₗ transition to be dominated by the HOMO → LUMO + 1 configuration (corresponding to a LUMO → LUMO + 1 one-electron transition from the HOMO → LUMO reference). In contrast, TDDFT favors the double HOMO to LUMO configuration. Correspondingly, the transition exhibits different oscillator strengths, with RASSCF/RASPT2 predicting a nearly 3 times larger value. The second state that can be reached from S₁ is much darker than the one discussed above at both levels of theory. This state has different symmetries and nature in the two calculations, and it appears in a region dominated by the S₁ SE signal, interfering with it.

The vibrational modes displaying large coupling to the S₀ → S₁ electronic transition are listed in Table 2, where the strength of the coupling is presented in terms of mode-specific reorganization energies. For the transition between S₀ and higher-lying states, only the total reorganization energy is reported. The reorganization energy is obtained projecting the excited-state gradients along the normal modes. Modes with large couplings are readily recognized by looking at the spectral densities shown in Figures S6 and S7 of the Supporting Information. In the frequency range below 1000 cm⁻¹, one mode around 550/650 cm⁻¹ couples strongly with the electronic structure. Interestingly, while at both levels the mode describes a symmetry-conserving breathing deformation, the motion is longitudinal at the RASSCF/RASPT2 level, whereas it is transversal at the TDDFT level. In the high-frequency range (above 1000 cm⁻¹), three/four main normal modes exhibit notable couplings, all related to symmetric C=C stretching and C–H bending. The modes are depicted in Figure S5 of the Supporting Information.

The high-frequency modes are more strongly coupled at the TDDFT level compared to that at the RASSCF/RASPT2 level, resulting in a 50% higher total reorganization energy of the S₀ → S₁ transition. As we will demonstrate in the next section, this discrepancy affects the relative intensities of the vibronic bands in the linear and nonlinear spectra. In contrast, transitions to the higher-lying states exhibit stronger couplings to the vibrational modes at the RASSCF/RASPT2 level: since numerical SS–RASPT2 gradients were calculated, a possible overestimation of the coupling has to be expected when multiple states lie close in energy at the RASSCF level (due to state swapping and mixing that may occur in the energy evaluation at the displaced geometries). This issue may be alleviated by using different flavors of multireference perturbation theory, such as the multistate (MS) and the extended multistate (XMS)-RASPT2. Again, this overestimation affects the broadening and relative intensity of the ESA features in the nonlinear spectra.

### 4.2. Optical Spectroscopy

In this section, we compare the experimental data with the simulations obtained at the RASSCF/RASPT2 and TDDFT levels of theory, following the spectral simulation methodology presented in Section 2.1 and extensively discussed in ref 10. In particular, we show

- the LA spectrum;
- the TA spectra;
- 2DES maps at different waiting times tₛ;
- Fourier transform maps of the oscillatory component of the TA signal, aimed at resolving the vibrational dynamics.

#### 4.2.1. Linear Absorption

The LA spectrum for the neutral PBI, as compared to the experimental one for the PBI-(R⁺)₂ monomer in acetonitrile, is shown in Figure 2. As already mentioned, test calculations on the PBI-(R⁺)₂ were also performed, and the simulated absorption spectrum for the cationic species is shown in Figure S1 of the Supporting Information.

![Figure 2](https://doi.org/10.1021/acscjctc.1c00570) J. Chem. Theory Comput. 2021, 17, 7134–7145
Information, showing negligible differences with the neutral PBI. This result is ultimately dictated by the presence of an identical photoactive region. For this reason, all the simulations of ultrafast spectroscopy were performed on the computationally cheaper neutral molecule.

Both the measured and simulated spectra display a structured spectrum in the 550–400 nm spectral range, identified as the vibronic absorption of the bright S\textsubscript{1} state peaking at ca. 520, 485, 455, and 425 nm, corresponding to the fundamental (i.e., 0-0) and the first three overtones (0-1, 0-2, and 0-3). The pronounced vibronic peaks result from a few strongly coupled high-frequency normal modes described in Section 4.1. The agreement between the spectra is substantial. The simulated spectra overestimate slightly the splitting of the bands, a possible explanation being the choice not to phenomenologically downscale the normal mode frequencies as often done. Furthermore, the RASSCF/RASPT2 underestimates, whereas the TDDFT overestimates the coupling to the vibrational modes (as already observed in ref 26), which affects the intensity of the overtones with respect to the experiment. Finally, we note that the simulated spectra have been blue-shifted by 1200 cm\textsuperscript{-1} (RASSCF/RASPT2) and 2800 cm\textsuperscript{-1} (TDDFT) to match the position of the experimental 0-0 peak. This difference may be ascribed (at least in part) to differences between the neutral PBI and the PBI-(R\textsuperscript{+})\textsubscript{2} S\textsubscript{1} state energy, the latter of which resulted being 700 cm\textsuperscript{-1} higher at the RASSCF/RASPT2 level (see the Supporting Information). Moreover, missing solute–solute electrostatic and polarization effects may also affect the molecule electronic structure calculations (which were performed here in the gas phase), as highlighted in a detailed analysis in ref 26. The above-mentioned shifts have also been systematically applied to the nonlinear spectra to facilitate the comparison between experiments and simulations.

4.2.2. Transient Absorption. Figure 3 reports experimental and simulated TA maps, resolved in the 100–600 fs window after the interaction with the pump pulse. The 0–100 fs window is not shown as it is contaminated by coherent artifacts due to temporal pulse overlap.

The agreement between experimental and theoretical spectra is evident as follows: at 525 nm, one observes contributions from both the GSB and the first band of the vibronic progression of the SE, while the second band of the SE lies around 575 nm. These values also match the vibronic peak energies recorded in the steady-state emission spectrum of a PBI derivative.
The beating frequencies revealed in the power spectra are consistent in the three maps and can be associated to the vibrational modes listed in Table 2. The frequency profile encompasses the breathing mode at around 540 cm$^{-1}$ and a couple of high-frequency bands at around 1300 and 1390 cm$^{-1}$, assigned to symmetric C=C stretching and C–H bending. We note that accounting for the finite duration of the experimental pulses is crucial in order to properly describe the relative intensity of the beating peaks in the power spectra. The finite temporal resolution sets a limit to the highest frequency detectable in the experiments below 1600 cm$^{-1}$. If the finite resolution is not accounted for, the calculated power spectrum becomes dominated by the higher-frequency peaks due to their higher Huang–Rhys factors as listed in Table 2. A comparison between simulated maps with finite- and infinite-time resolution is shown in Figure S9 of the Supporting Information.

A few differences between experimental and simulated power spectra are worth noting. First, one observes that the peaks in the simulated maps are broader along the frequency axis. In fact, in the analysis of the experimental data, all decaying components were subtracted prior to the Fourier transform step, while in the theoretical data, this subtraction was not performed. Furthermore, one can observe that the RASSCF/RASPT2 computational level reproduces frequencies and intensities more accurately with respect to TDDFT, which gives rise to a significant blue shift of the high-frequency peak energy and overestimates the weight of the 1600 cm$^{-1}$ mode (cf. Table 2).

Finally, the absence of peaks above 530 nm in the experimental power spectra can be ascribed to the limited bandwidth of the experimental pump pulse resonant with the 0-0 transition which suppresses to a great extent the excited-state vibrational dynamics during $t_2$.

4.2.4. 2DES. 2DES is capable of providing additional information regarding the time scale of spectral diffusion as it correlates the probe wavelength to the pump wavelength, effectively increasing the spectral resolution. We performed simulations of 2DES at a few selected waiting times. A comparison of the computed maps to those measured in the experiment is shown in Figure 5.

Figure 5. Comparison between (a) experimental and (b,c) simulated 2DES maps at few waiting times $t_2$ at the RASSCF/RASPT2 and TDDFT levels of theory. The experiments report results for the PBI-(R$^+$)$_2$ in acetonitrile, while the simulations were performed on the PBI neutral molecule in the gas phase. The simulated spectra have been shifted by 1200 and 2800 cm$^{-1}$. Their intensity was scaled to match the experimental one, allowing us to use an identical intensity window and color range for the three sets of data. GSB and SE are shown in red and ESA in blue.
experimentally is shown in Figure 5. In the experiment, a diagonal band in the 2DES at ca. 525 nm is associated with the GSB and SE of the 0-0 line, whereas two cross-peaks from the vibronic progression of the SE are detected at ca. 570 (also seen in the TA spectrum) and 615 nm. An ESA cross-peak appears almost simultaneously after the interaction with the pump pulse pair, centered around 700 nm on the detection axis (shown in blue), extending from ca. 625 nm to the red side of the spectrum. This signal originates as a photoinduced absorption from the S1 state prepared by the pump pulse and can be identified with the most intense transitions listed in Table 1 (i.e., S1 \( \rightarrow \) S2 at the RAS level or S1 \( \rightarrow \) S3 at the TDDFT level). Note that a different pulse shape was employed here with respect to the previously reported TA spectrum; such a pulse shape extends the probe bandwidth in the red to 750 nm allowing us to clearly capture the photoinduced absorption, whose weak tail was only faintly visible in the TA spectrum (see Figure S8 in the Supporting Information).

The main experimental peaks are successfully reproduced by the simulations; however, some discrepancies are apparent. The RASSCF/RASPT2 ESA peak appears strongly broadened, spreading in the range 600–750 nm. As a consequence, it is also less intense. This spread can be rationalized in part by the large reorganization energy found for state S7 (at the RAS level or S7 at the TDDFT level), which may be overestimated in numerical SS-RASPT2 gradient calculations, and also partially by the neglect of the finite pulse bandwidth in the simulation. A refined treatment of the limited experimental bandwidth, in resonance almost exclusively with the first vibronic band of the absorption, would produce a cold wavepacket at the bottom of the S1 well. In contrast, the \( \delta \)-pulse used in the present experiments leads to an excess of kinetic energy of the wave-packet, which eventually broadens the ESA peak. Note how, in the case of the RASSCF/RASPT2 results, this broadened ESA peak partially covers the third peak of the S1 SE vibronic progression, which is instead clearly visible around 615 and 625 nm in the experimental and TDDFT maps, respectively. Note also that this peak is much stronger in the TDDFT maps than in the experiment due to the overestimation of the S0 \( \rightarrow \) S1 vibronic coupling at the TDDFT level.

Regarding the signal dynamics along \( t_2 \), we observe a marked spectral diffusion, characterized by the progressive circularization (i.e., loss of correlation between the pump and probe) of the initially elongated peaks at 525 and 575 nm emission wavelengths following the memory loss in the system due to the solvent reorganization around the PBI molecule. This effect can be captured by a number of quantitative measures (flattening, ellipticity, central line slope, etc.). Here, we employed the flattening parameter, obtained as the difference between the diagonal and antidiagonal widths of a peak, normalized to the diagonal width. The evolution of the flattening parameter for the diagonal peak as a function of the waiting time \( t_2 \) is shown in Figure 6 for both experiments (a) and simulations (b,c). Note that the initial flattening value is larger in the experiment as the experimental peak is tilted more strongly at early times. An exponential fit of the decay of the flattening provides the time scale \( \tau \) of the solvent reorganization, being ca. 40 fs in theory and experiment. As the simulations were performed in the gas phase, this phenomenon was introduced through the OBO spectral density whose time-scale parameter \( \Lambda^{-1} \) was chosen precisely as 40 fs (see Section 2.1) to reproduce the fastest experimental time scale. This value can also be obtained evaluating the solvent-induced energy gap fluctuation along a molecular dynamics simulation. Notably, the experimental flattening does not decay to zero at longer times (250 fs) at variance with the simulations. This suggests the presence of a second, slower relaxation time scale, which was not modeled in the simulations. Note that the presence of a fast and slow time scale for the acetonitrile relaxation dynamics has been reported in the literature in both theoretical and experimental studies. Finally, the flattening is observed to oscillate along the \( t_2 \) time, and the Fourier analysis of these oscillations returns the same intramolecular beating frequencies discussed above.

5. CONCLUSIONS

This paper demonstrates the power of in silico spectroscopy to reproduce, interpret, and, in some cases, predict experimental ultrafast optical spectroscopy data. We reported the simulation of linear and nonlinear spectroscopy of the neutral PBI at two levels of theory, namely, RASSCF/RASPT2 and TDDFT. The obtained results were compared with experiments performed in acetonitrile.

While the RASSCF/RASPT2 approach is well-known for being capable of simulating nonlinear spectroscopy from first principles, the present work shows that, in principle, a TDDFT protocol can be also adapted for the same purposes. The calculated PBI spectra at both levels of theory show a remarkable agreement with the experimental data. These include LA (which probes the vibronic structure of the first singlet excited state, S1) and nonlinear techniques such as TA and 2DES (for which a reliable description of higher-lying states is crucial). Both static (signals positions and intensities) and dynamical spectral properties (such as intensity beating and
The microscopic origin of the main spectral features of PBI in solution is demonstrated as follows: the beating frequencies are assigned to specific molecular Raman-active modes. The importance of incorporating the finite time resolution and limited bandwidth of the experiment in the simulations is also discussed.

A detailed comparison of the QC sets of data obtained at the two levels of theory was carried out, demonstrating that TDDFT with a relaxed singly excited configuration as reference succeeds in capturing states with a doubly excited-state character, elusive to standard (ground state) TDDFT. Moreover, dipolar couplings between excited states can be computed straightforwardly (within a pseudowavefunction representation), thereby rendering accessible all the quantities required to simulate nonlinear spectra.

We note that the TDDFT approach may encounter convergence issues when the reference state is not dominated by single configurations. Furthermore, it remains blind to high-lying states described through multiple excitations out of the reference state (i.e., states dominated by triple- or higher-order excitations), which nonetheless will in general produce negligible contributions in the simulated spectra. Photoexcited molecules evolving to states of doubly excited nature will instead continue to pose a challenge. Future work in this direction will be carried out to demonstrate the performance of the method and its range of applicability in diverse molecular systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.1c00570.

Summary of the parameters employed in the spectroscopy simulations; configurations of TDDFT states; PBI and PBI-(R⁺); LA spectra; RASSCF active space orbitals, and excited-state energies; PBI-relevant DFT orbitals; normal modes at the MP2 and DFT levels of theory; spectral densities of the bright transitions; shape of the experimental laser pulses; TA spectrum for GSB, SE, and GSB + SE contributions; Fourier analysis of TA data with finite and infinite resolution; Fourier analysis of TA data for GSB, SE, and GSB + SE contributions; and cuts of the 2DES spectra at selected t2 times (PDF)

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Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTE

“The coupling with modes below 300 cm⁻¹ was set to zero.

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Supporting Information

for

In silico ultrafast nonlinear spectroscopy meets experiments: the case of perylene bisimide dye

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This PDF includes:

- Summary of the parameters employed in the spectroscopy simulations;
- Configurations of TDDFT states: comparison of different representations;
- PBI and PBI-(R⁺)₂ linear absorption spectra;
- PBI and PBI-(R⁺)₂: RASSCF active space orbitals and excited state energies;
- PBI relevant DFT molecular orbitals;
- Normal modes at the MP2 and DFT level of theory;
- Spectral densities of the bright transitions;
- Shape of the experimental laser pulses and their overlap with the (experimental) linear absorption spectrum;
- TA spectrum for GSB, SE, and GSB+SE contributions;
- Fourier Analysis of TA data with finite and infinite resolution;
- Fourier Analysis of TA data for GSB, SE, and GSB+SE contributions;
- Cuts of the 2DES spectra at selected \( t_2 \) times.
S1 Summary of the parameters employed in the spectroscopy simulations

Simulations were carried on with $t_2$ in the interval (0, 600) fs. In fact, the relevant dynamics happens before 600 fs, and 600 fs upper limit is long enough to safely perform the Fourier transform of the low frequency modes.

The time delay between consecutive $t_2$ points was set to 4 fs. This is short enough to allow proper sampling of the high-frequency modes (so that they can be revealed by Fourier transform of the data), but also long enough to reduce the number of $t_2$ snapshots to be evaluated.

Other parameters include the OBO $\lambda$ and $\Lambda^{-1}$ values, set to 240 cm$^{-1}$ and 40 fs respectively, and whose meaning has been explained in the main text.

As discussed in the main text, the lifetime of the $S_1$ state was set to infinity (i.e. very long compared to the time scale of the simulations reported here). This allows to use analytic expressions for the response functions.
S2 Configurations of TDDFT states: comparison of different representations

The following Table reports on the leading configuration (weight > 0.05) of the states involved in the bright transitions. Two different representations are compared: the one directly obtained from the calculations (in which the HOMO → LUMO configuration is used as a reference), and one in which the closed shell GS configuration is used as a reference. The latter was also employed in Table 1 of the main text, as it makes the comparison with RASSCF/RASPT2 simpler. To make an example, the HOMO → LUMO transition from the HOMO → LUMO reference, corresponds to a HOMO ⇒ LUMO from the closed-shell reference; the HOMO−3 → HOMO transition from the HOMO → LUMO reference, instead, corresponds to a HOMO−3 → LUMO transition.

Table S1: Comparison of TDDFT leading configurations (weights > 0.06) of the states involved in the transitions, for a) the GS (closed-shell configuration) as reference, and b) the S1 state (HOMO → LUMO configuration) as reference. Single and double arrows denote single and double occupied to virtual transitions, respectively. The orbital are labeled consistently to their depiction if Figure S4.

| Transition | State Symm. | Arrival St. Config. (GS ref.) | Arrival St. Config. (S1 ref.) | Weight |
|------------|-------------|-------------------------------|-------------------------------|--------|
| S0 → S1    | A_g → B_{3u} | HOMO → LUMO                   | -                             | 0.92   |
| S1 → S5    | B_{3u} → A_g | HOMO ⇒ LUMO                   | HOMO → LUMO                   | 0.38   |
|            |             | HOMO−3 → LUMO                 | HOMO−3 → HOMO                 | 0.36   |
|            |             | HOMO → LUMO+1                 | LUMO → LUMO+1                 | 0.21   |
| S1 → S7    | B_{3u} → B_{1g} | HOMO−4 → LUMO               | HOMO−4 → HOMO                 | 0.45   |
|            |             | HOMO → LUMO+2                 | LUMO → LUMO+2                 | 0.42   |
Figure S1: Linear absorption (vibronic) spectra of PBI (red) and PBI-(R^+)_2 ion (blue) computed at RASSCF/RASPT2 level of theory; due to the computational cost of the MP2 method, frequencies has been computed at DFT level (using ωB97X-D functional and 6-31G** basis-set). To match the experimental λ_{max} of a 1 mM solution of PBI-(R^+)_2 in acetonitrile (black curve), the computed spectra have been blue-shifted by +1200 cm^{-1} (PBI) and +400 cm^{-1} (PBI-(R^+)_2). Upon normalization to the maximum of the first vibronic band, the successive vibronic bands of PBI-(R^+)_2 ion are more intense with respect to those of the neutral PBI and closer to the experimental spectra. The total reorganization energy for the S_1 state in PBI-(R^+)_2 is 960 cm^{-1}.
S4  PBI and PBI-(R^+)_2: RASSCF active space orbitals

Figure S2: SA-10-RAS(20,4,4;10,0,10) natural orbitals used for multireference calculations on PBI-(R^+)_2 ion. Natural orbitals are grouped according to the irreducible representations of C_{2h} symmetry point group.

Figure S3: SA-10-RAS(20,4,4;10,0,10) natural orbitals used for multireference calculations on PBI (neutral) molecule. Molecular orbitals are grouped according to the irreducible representations of D_{2h} symmetry point group.
S5  PBI and PBI-(R\(^+\))\(_2\): RASPT2 excited state energies

Table S2: The lowest ten electronic states were considered for all allowed symmetries (four) of the C\(_{2h}\) and D\(_{2h}\) point groups of PBI and PBI-(R\(^+\))\(_2\). Here we report the states transition energy at the SS-RASPT2 level. The PBI S\(_0\), S\(_1\), S\(_7\) and S\(_{12}\) and the PBI-(R\(^+\))\(_2\) S\(_0\) and S\(_1\) states are highlighted in bold. Transition dipole moments were computed for relevant transitions allowed by symmetry, i.e. A\(_g\) → B\(_{2u}\)/B\(_{3u}\) and B\(_{3u}\) → A\(_g\)/B\(_{1g}\) for PBI, and A\(_g\) → A\(_u\)/B\(_u\) and B\(_u\) → A\(_g\)/B\(_g\) for PBI-(R\(^+\))\(_2\). The brightest transitions have been reported in the main text.

| State | PBI | PBI-(R\(^+\))\(_2\) |
|-------|-----|---------------------|
|       | \(A_g\) (eV) | \(B_{3u}\) (eV) | \(B_{2u}\) (eV) | \(B_{1g}\) (eV) | \(A_g\) (eV) | \(B_g\) (eV) | \(A_u\) (eV) | \(B_u\) (eV) |
| 1     | 0.00 (S\(_0\)) | 2.35 (S\(_1\)) | 3.31 | 3.07 | 0.00 (S\(_0\)) | 3.18 | 3.41 | 2.45 (S\(_1\)) |
| 2     | 3.08 | 4.52 | 4.48 | 3.40 | 3.32 | 3.51 | 4.67 | 4.69 |
| 3     | 4.13 (S\(_7\)) | 4.84 | 4.64 | 3.48 | 4.06 | 3.58 | 4.73 | 4.91 |
| 4     | 4.44 | 5.41 | 5.01 | 4.29 | 4.75 | 4.20 | 5.03 | 5.60 |
| 5     | 4.51 (S\(_{12}\)) | 5.28 | 4.48 | 4.63 | 4.59 | 4.91 | 4.66 | 5.32 |
| 6     | 5.16 | 5.66 | 5.21 | 5.55 | 5.35 | 5.73 | 5.31 | 5.61 |
| 7     | 5.47 | 6.15 | 5.67 | 5.92 | 5.58 | 6.11 | 5.83 | 6.08 |
| 8     | 5.87 | 5.68 | 5.53 | 5.83 | 6.07 | 5.91 | 5.70 | 5.93 |
| 9     | 5.99 | 5.57 | 6.62 | 5.91 | 6.16 | 6.14 | 6.82 | 5.60 |
| 10    | 6.15 | 6.45 | 6.09 | 6.56 | 6.28 | 6.63 | 5.93 | 6.73 |
Figure S4: Relevant DFT molecular orbitals for $S_1$, $S_5$ and $S_7$ excited states of PBI (isovalue 0.01). Molecular orbitals are grouped according to the irreducible representations of $D_{2h}$ point group. The orbitals are labeled in two ways: the black label below each molecular orbital refers to the RASSCF assignation of Figure S3 (which facilitate the comparison of the states configurations of Table 1 in the main text), while the grey label in parentheses refers to the original DFT ordering.
S7  Analysis of normal modes and frequencies

Figure S5: Selected normal modes computed at MP2 and DFT level of theory. For each normal mode, the corresponding frequency (in cm\(^{-1}\)) is also reported in parenthesis. All normal modes reported here are of \(A_g\) symmetry (i.e. total symmetric modes).
S8  Spectral densities

S8.1  \( J(\omega) \) for the \( S_1 \) state

Figure S6: Spectral densities for the \( S_0 \rightarrow S_1 \) transition at TDDFT (blue) and RASSCF/RASPT2 (red) level of theory. The arrows highlight the PBI breathing modes that are responsible for the low frequency beatings observed in the power spectrum. The overdamped brownian oscillator spectral density \( (J_{OBO}(\omega)) \) with \( \lambda = 240 \text{ cm}^{-1} \) and \( \Lambda^{-1} = 40 \text{ fs} \) is also reported (black line).

S8.2  \( J(\omega) \) for the \( S_7 \) (\( S_5 \)) RASSCF/RASPT2 (TDDFT) state

Figure S7: Spectral densities for the transitions that gives rise to the brightest ESA signal in the nonlinear spectra, namely: \( S_1 \rightarrow S_5 \) at TDDFT level (blue line), and \( S_1 \rightarrow S_7 \) at RASSCF/RASPT2 level (red line).
Figure S8: Experimental linear absorption spectrum of PBI (black) and pulse shapes used in the experiments. The blue pulse shape was used for TA, while the red pulse shape was employed in 2DES experiments. Note how the latter covers a region in which the ESA signals are observed, therefore allowing for their detection.
Figure S9: (a,b) GSB, (c,d) SE and (e,f) TOTAL TA maps at both RASSCF/RASPT2 and TDDFT levels of theory. The ability of selectively switching on and off different contributions of the total TA map, allows to untangle and label the origin of the observed signals, also in regions where these may overlap (as it happens around 525 nm).
S11  Fourier Analysis with infinite and finite time resolution

Figure S10: Fourier analysis of the TA maps at the two levels of theory, with finite (a-b) and infinite (c-d) time resolution. Note that the high frequency modes appear quenched when (realistic) finite resolution effects are included. The longer the pulse width in time, the lower the resolution, the larger the quenching of the high-frequency beatings peaks is.
Figure S11: (a,b) GSB, (c,d) SE and (e,f) TOTAL Fourier transformed TA maps at both RASSCF/RASPT2 and TDDFT levels of theory. Note that the GSB and SE contributions give rise to peaks in different regions of the map. Note also the different position of the horizontal nodes, located at ca. 520 and 530 nm in the GSB and SE maps, respectively, i.e. at the maxima of the absorption and emission spectra.
Cuts of the 2DES spectra at selected $t_2$ times

Figure S12: Comparison of some cuts of the 2DES maps reported in Figure 5 of the main text, for both experiment and simulations. The cuts were performed at Excitation wavelength equal to 530 nm, and for the $t_2$ times 10, 30, 50, 70 and 90 fs. The main qualitative features of the experiment are reproduced in the simulations, while quantitative differences can be noticed in terms of peak position (minor red-shift of the SE progression at both levels of theory, and blue-shift of the ESA peak at the TDDFT level) and line-shape (excess of broadening of the main GSB/SE peak at early times at both levels of theory, and for the ESA peak at all times at the RASSCF/RASPT2 level).