Ultrafast bi-excitonic dynamics and annihilation in molecular and mesoscopic systems

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Abstract. We present 5th and 3rd order 2D spectra of a squarine trimer. Slowly decaying (τ = 0.8 ps) and intensity dependent features unique to the 5th order signal are attributed to exciton-exciton annihilation.

1 Introduction

At high light intensities, several excitations can be induced within a single absorber and the process known as exciton-exciton annihilation (EEA) may become an essential part of the observed dynamics. EEA is a two-exciton interaction process, in which excitation energy is transferred resonantly between two neighbouring sites in their first excited state (S_1), lowering one site to the ground state (S_0) while promoting the other to a higher-lying singlet state (S_n). Deactivation pathways of S_n can include non-radiative decay, charge separation etc. [1]. The outcome of the process is the effective loss of one excitation quantum. Since EEA can be efficient even at relatively low fluences, a better understanding of multiple exciton effects is essential for reconstructing annihilation free spectroscopic signals. Conventionally, EEA is probed by measuring the intensity dependence of the 3rd order nonlinear signals ,$R^{(3)}$, such as pump-probe [2], which is however an indirect approach in need of subsequent modelling. So-called double quantum two-dimensional electronic spectroscopy (2Q-2D) addresses bi-excitonic states relevant for EEA directly [3]. However, its realization is experimentally challenging, primarily due to the required phase stability of all three excitation pulses. More critically, the signal only persists for the duration of pulse overlap and hence suffers from the pulse-related artefacts [4]. Here we present a novel experimental approach for direct probing of bi-excitonic states and their lifetimes by detecting 5th order non-linear signals ($R^{(5)}$). The experiment is the fully non-collinear version of the shaper-based approach recently presented by Dostal et al. [5]. Its main advantage over 2Q-2D is that the system is promoted into a population state during the waiting period, which leads to signals that are more robust. Therefore, the effects of EEA can be studied explicitly instead of just indirectly via 3rd order intensity dependences. The

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method was tested on a molecular system consisting of three identical squaraine dye subunits (tSQA), synthesized according to the published procedures [6].

2 Experimental setup

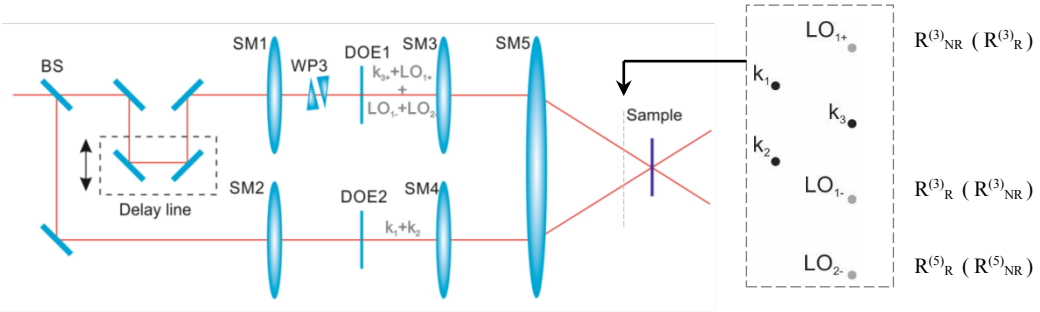

Fig. 1. (a) Schematics of the experimental setup. DOE – diffractive optic element; WP – wedge pair, SM – spherical mirror, BS – beam splitter (b) Actual boxcar geometry for measuring $R^{(3)}$ and $R^{(5)}$-signals, heterodyned with local oscillators LO_{1-}, and LO_{2-}, respectively. Depending on the relative time-ordering of $\mathbf{k_1}$ ($\mathbf{k_2}$), the measured 2D spectra are either of rephasing (index R) or non-rephasing (NR) character, but emitted along the same phase-matching direction

Fig. 1 shows the schematics of the experimental setup, which represents the $R^{(5)}$ extension of a previously published $R^{(3)}$ setup [7]. In brief, the initial 570 nm / 8 fs pulse is generated by a home-built non-collinear parametric amplifier (NOPA) [8] and is split by a 50:50 beamsplitter (BS). The transmitted pulse is translated by a computer controlled linear motorized stage to introduce delay t_2. Both pulses from the BS are then focused by separate spherical mirrors (SM1 and SM2, radius of curvature R = 750 mm) onto diffractive optical elements (DOE1 and DOE2). The diffracted beams are collimated by another pair of spherical mirrors (SM3 and SM4, radius of curvature R = 600 mm). Wedge pairs WP1 and WP2 are used to introduce a delay t_1 between beams along $\mathbf{k_1}$ and $\mathbf{k_2}$. Both WPs show a 2° apex angle and are made of fused silica, with one of the wedges in each pair being stationary and another mounted on a linear motorised stage. Wedge pair WP3 is used to balance dispersion of pulses along $\mathbf{k_3}$ and local oscillator beams. The intensity of all beams can be independently adjusted by a neutral density filters. All beams derived from the same DOE traverse by the same optics to keep the pulses locked in phase. All the interacting beams are focused onto the sample by a spherical mirror SM5 (radius of curvature R = 750 mm).

Switching from $R^{(3)}$ to $R^{(5)}$ is readily achieved by detecting in the appropriate phase matching direction in a fully non-collinear and hence background-free folded boxcar geometry. The 3rd order signal is detected along $\mathbf{k_{wR3-}} = -\mathbf{k_1}+\mathbf{k_2}+\mathbf{k_3}$, (which is the direction of the local oscillator $\mathbf{LO_{1-}}$ in figure 1), while the 5th order signal propagates along $\mathbf{k_{wR5-}} = -2\mathbf{k_1}+2\mathbf{k_2}+\mathbf{k_3}$ (direction of $\mathbf{LO_{2-}}$). Both signals were detected in the shot-to-shot regime with CCD-cameras operating at 50 kHz.

3 Results and discussion

We have measured rephasing and non-rephasing $R^{(3)}$ and $R^{(5)}$ signals. $R^{(3)}$ signals were phased to pump-probe signal in accordance to projection slice theorem. Global analysis of a series of measurements as a function of t_2 revealed two exponential decays of τ_1 = 16 fs and $\tau_2 >> 1$ ps for the $R^{(3)}$ signal and three exponential decays (τ_1 = 16 fs, τ_2 = 830 fs,

τ_3 >> 1 ps) in the $R^{(5)}$ case. We attributed the extra 0.8 ps decay time to EEA. Due to higher number of interactions, fifth order signal is even more sensitive to molecule structure than third order signal. Computer simulations showed that elongation of the 5th order signal along ω_1 coordinate is not possible in a trimer with linear configuration, revealing that the investigated squarine trimer is more likely taking the U-shaped form.

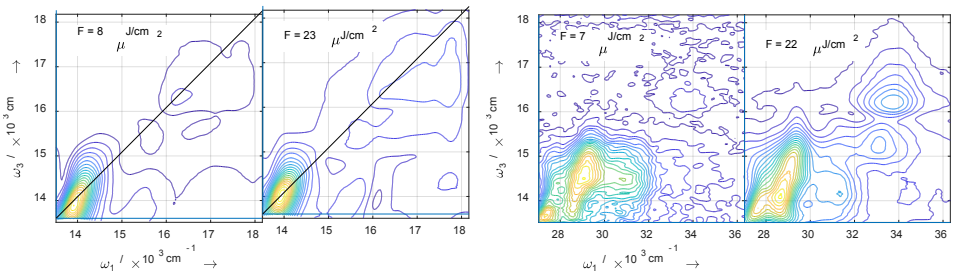

Fig. 2. Amplitude of evolution associated decay spectra (EADS, τ = 16 fs) of 3rd (a) and 5th (b) order signals at two different pulse energies indicated on the maps. Note the different ω_1 ranges in (a) and (b), indicating the selectivity for double excitonic states in 5th order signals.

4 Conclusions

We demonstrate an experimental design for measuring 5th order signals without employing pulse shapers and in a fully non-collinear boxcar geometry. We show that 5th order measurements address the bi-excitonic manifold in a molecular homo-trimer, with pronounced intensity dependent effects in $R^{(5)}$, but hardly any intensity dependence in $R^{(3)}$. Global analysis of the 5th order measurements reveal a 0.8 ps decay component, not present in the dynamics of the 3rd order signal. We attribute this additional decay time to EEA, or more precisely to the lifetime of the second excited manifold. Comparison of computer simulations discussed elsewhere and $R^{(5)}$ signal revealed that squarine trimers in mesitylene solution predominantly assume a U-shaped form.

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