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Manipulating Multidimensional Nonlinear Spectra of Excitons by Coherent Control with Polarization Pulse Shaping

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Abstract: Femtosecond two-pulse photon echo signals of excitons from a chiral porphyrin dimer are simulated using the CGF (cumulant expansion of Gaussian fluctuations) method. The spectra are disentangled using various optimization strategies for the spectral, temporal and polarization profiles of the pulse.

Multiple sequences of optical pulses with variable delays provide direct probes for electronic and vibrational motions [1,2]. Dynamical information may be extracted from the nonlinear signals of complex systems by displaying them in multiple dimensions [3]. We apply coherent control with polarization pulse shaping to amplify weak spectral features in 2D two-pulse photon echo (PE) signals of the Soret band of a chiral porphyrin dimer.

We have carried out optimization of the heterodyne 2D two-pulse photon spectra of a chiral porphyrin dimer (Fig. 1, A).

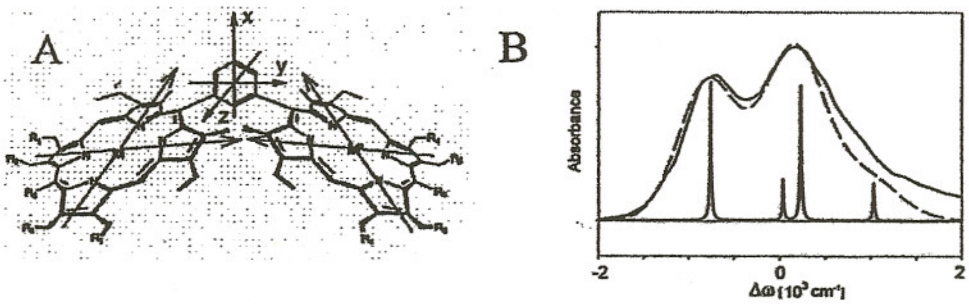

Fig. 1. (A) Chemical structure of a porphyrin dimer. (B) Linear absorption: experimental spectrum (solid) [4]; simulated spectra with the linewidth 10 (thin solid), and 486 cm^{-1} (dashed).

The dimer has two coupled pairs of perpendicular transition dipoles. We used the Frenkel-exciton Hamiltonian in the Heitler-London approximation with structure parameters reported by Won et al [4]. The overdamped Brownian oscillator model in the high temperature limit was used for line broadening [1]. The experimental linear absorption was fitted using the following parameters: the fluctuation magnitude $\Delta = 145$ cm^{-1}, and the relaxation rate $\Lambda = 160$ cm^{-1}at room temperature. We calculated the $\mathbf{k_I} = -\mathbf{k_1} + \mathbf{k_2} + \mathbf{k_3}$ signal using Eq. 10.13 of [5]. The signal in the dipole approximation has three tensor components: Wxxyy, Wxyxy, Wxyyx, where x and y refer to the polarizations of the electric fields.

Fig. 1, B shows the simulated linear absorption spectra with linewidths of 10 (thin solid line) and 486 cm^{-1} (dashed line), and the experimental spectrum (solid line) [4]. The 2D two-pulse PE spectra are shown in Fig. 2, A. The unoptimized 2D spectra with initial Gaussian pulses with σ = 6111 cm^{-1} (top row) has two intense diagonal peaks, and weak cross peaks (marked with circles).

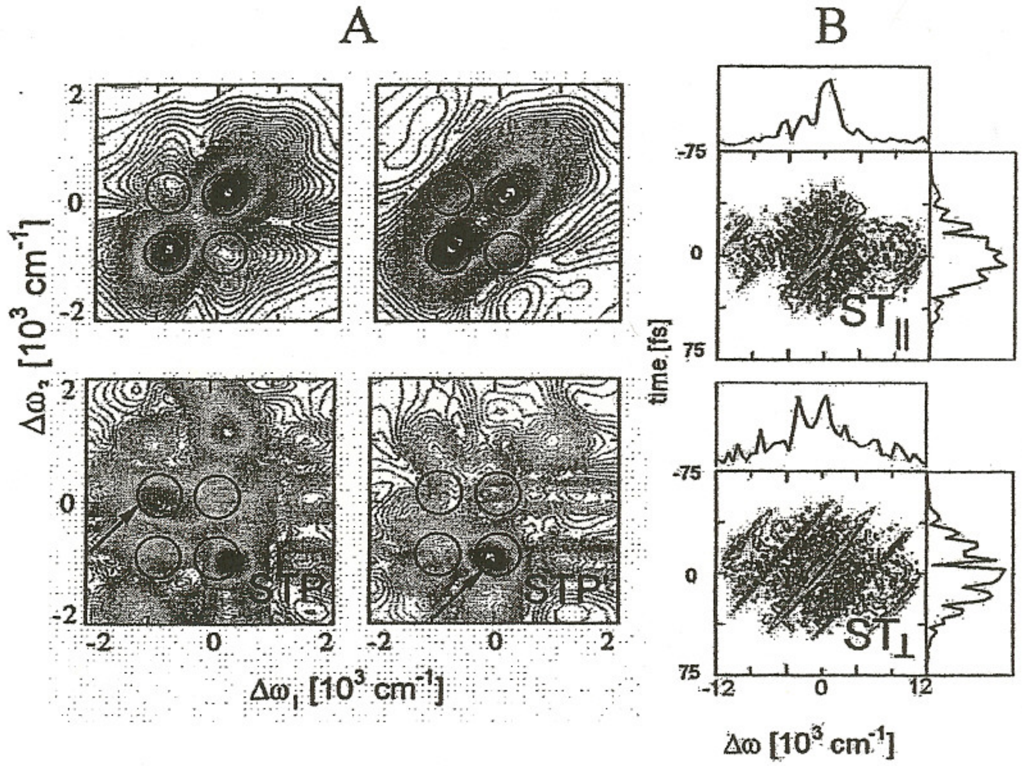

Fig. 2. (A) Optimized two-pulse photon echo spectra: (top row) Wxxxx (left) and Wxyyx (right) using initial laser pulses; (left column) optimized T1; (right column) optimized T2 (absolute part, arrows indicate the optimized peaks). (B) Wigner spectrograms and corresponding spectral and temporal marginals of the optimized linearly polarized pulses.

We defined the control targets T_1 and T_2 as the ratios of the integrated cross peaks (-770 cm^{-1}, 150 cm^{-1}) and (150 cm^{-1}, -770 cm^{-1}), respectively, to the integrated diagonal peaks at (-770 cm^{-1}, -770 cm^{-1}) and (150 cm^{-1}, 150 cm^{-1}) (Fig. 2, A). Four pulse shaping forms for the second pulse were used for the optimization of T_1. The first two forms, $ST_{\parallel}$ and $ST_{\perp}$, involve spectral and temporal shaping of parallel and perpendicular linearly polarized pulses, respectively. The third form P uses pure-phase polarization pulse shaping, using the iterative Fourier transform algorithm [6]. The fourth form STP involves temporal, spectral and polarization pulse shaping. We denote the corresponding optimizations of the T_2 target by $ST'_{\parallel}$, $ST'_{\perp}$, P', and STP'. The 2D spectra optimized using genetic algorithm [7] by the STP and STP' forms are shown in Fig. 2, A (bottom row). The Wigner spectrograms of the optimal linearly polarized pulses are given in Fig. 2, B. Quasi-three dimensional representations of the optimized laser pulse shapes STP and STP' are shown in Fig. 3.

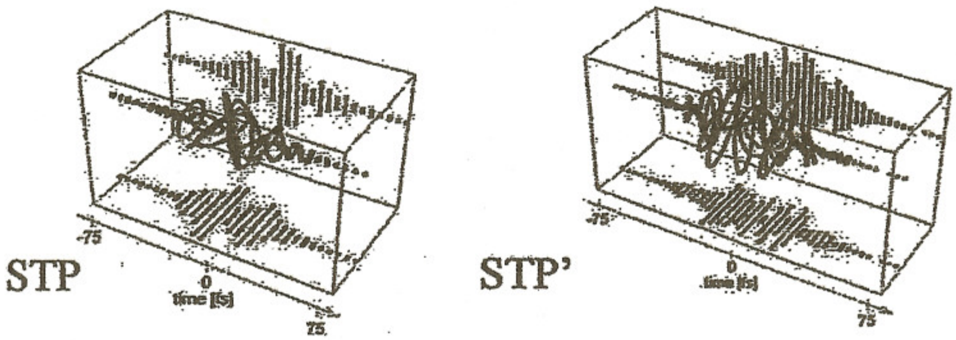

Fig. 3. Quasi-three-dimensional electric field representation of the optimized laser pulses STP and STP'.

The optimized electric fields with different polarizations select different Liouville space pathways of the tensor components of the response functions, which add coherently and interfere to obtain the total PE signal. Weak and congested cross peaks can be resolved, and diagonal peaks are suppressed [7]. We have demonstrated that the cross peaks can be manipulated to by varying different parameters of the electric field.

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