EPJ Web of Conferences **41**, 12006 (2013)
DOI: 10.1051/epjconf/20134112006

Nonlinear spectroscopy of chromophore aggregates with entangled photon pulses

F. Schlawin, K. E. Dorfman, B. F. Fingerhut, and S. Mukamel

Department of Chemistry, University of California, Irvine, California 92697-2025, USA

Abstract. The response of the bacterial reaction center to entangled photons is compared with stochastic and chirped pulses. Nonlinear optical signals reveal how distributions of exciton states may be controlled by quantum light.

1 Nonlinear spectroscopy with quantum light

Quantum light provides novel possibilities for nonlinear spectroscopy by tuning parameters of the photon wavefunction. Frequency-entangled photons possess various attractive features for spectroscopic applications. The coherent interaction of pairs of photons scales linearly in the pump intensity, thus allowing for much lower light intensities for nonlinear signals [1]. We show how frequency entanglement can be utilized to create exciton distributions in the bacterial reaction center *B. viridis* (Fig. 1A) that cannot be realized with classical pulses. The energy-time entanglement can be used to control population transport in the single-exciton manifold, while the broad bandwidth of the two photons (Fig. 1B) allows to explore all the pathways through the single-exciton manifold (see Fig. 1C, [2]). These effects are clearly seen in two-photon-induced fluorescence signals. The simulations are based on a tight-binding formulation of the electronic Hamiltonian, and incorporate excitation energy transfer as well as the coupling to charge-separated states [3].

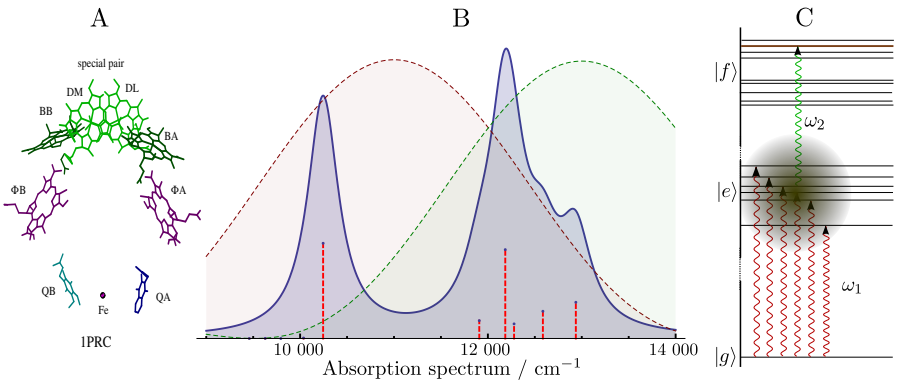

Fig. 1. A: The bacterial reaction center (PDB code: 1PRC). B: The linear absorption spectrum (blue) as well as the power spectrum of two entangled beams (red & blue dashed) with central frequencies $\omega_1 = 11\,000$ and $\omega_2 = 13\,000$ cm^{-1}. The exciton states are marked by dashed vertical lines whose height is proportional to their dipole moments. C: The broadband entangled beams allow to explore all pathways leading to a doubly-excited state through the single-exciton manifold.

2 Correlation functions of nonlinear signals

In nonlinear spectroscopy with laser pulses, the pulse spectral density (two-point correlation function of the field $\langle E^{\dagger}(t_1)E(t_2)\rangle$) determines the frequency- and time-resolution. In parametric down-conversion, a pump photon with frequency ω_p splits into two photons with ω_1 and ω_2, such that $\omega_p = \omega_1 + \omega_2$. The power spectrum of the two generated beams, as depicted in Fig. 1B, can be controlled by the crystal geometry, and it can be considerably broader than the generating pump spectrum. But although the power spectra of the two beams may be very broad, the sum of their frequencies can still be sharply peaked due to the energy entanglement. This feature shows up in higher-order correlation functions, $\langle E^{\dagger}(t_1)E^{\dagger}(t_2)E(t_4)E(t_3)\rangle$, which also determine third-order nonlinear signals.
We have considered excitation by three types of light: entangled photon pairs, classical chirped pulses, and stochastic light all having the same spectral density. Although the chirped pulses are designed to mimic the second- and fourth-order correlation function as closely as possible, the four-point correlation functions of the fields are very different for all three types of light.

3 Double-exciton distributions

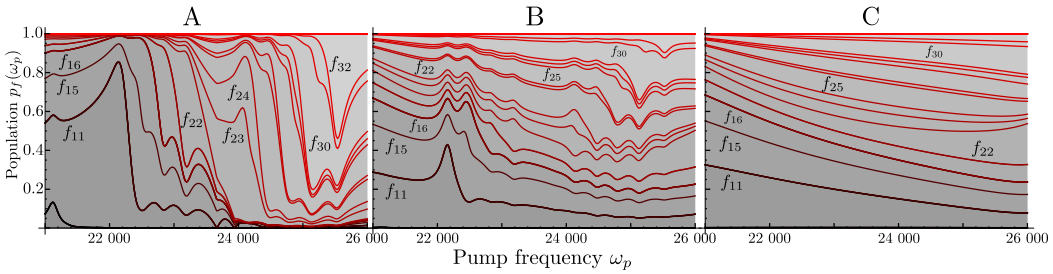

Fig. 2. The distribution of states in the double-exciton manifold $f_1 \ldots f_{41}$ created by entangled photons (A), chirped pulses (B), and stochastic light (C) are plotted vs. the pump frequency ω_p. The power spectrum corresponding to the chosen parameters is identical for all beams and shown in Fig. 1B.

The pump pulse duration determines the frequency entanglement, and the length of the nonlinear crystal fixes the spectral width of the power spectrum as well as the so-called entanglement time. In Fig. 2A, we present the distribution of double-excitons of the reaction center created by entangled photons with a pump beam with a 100 cm^{-1} bandwidth and entanglement time 10 fs. Tuning the pump frequency ω_p allows us to selectively excite specific double-exciton states. For stochastic light (Fig. 2C) the excited state distribution (Fig. 2C) is virtually independent of ω_p due to the broad bandwidth stemming from the short entanglement time. Chirped pulses can partially mimic the behavior of entangled photons (Fig. 2B). However, they also contain an incoherent contribution similar to the stochastic signal.

4 Control of population transport

In Fig. 3 we plot the populations of states f_{11} and f_{23} vs. the pump frequency and the entanglement time. While the pump frequency controls the state distribution (see Fig. 3), the entanglement time can further control transport in the e-manifold. As depicted in Fig. 3C, the state f_{11} gets populated mainly via the single-exciton state e_5, and f_{23} through e_6 as well as - less strongly - via e_7 and e_8. Coupling between the chromophores transfers the population of of higher-energy states such as e_6 to e_5 within $\sim$ 100 fs. Figs. 3A & B show how we can control this transport through the entanglement time T, which sets an upper bound on the length of time the system spends in the single-exciton manifold. As we increase T, the f_{23}-resonance around $\omega_p \sim 24000$ cm^{-1} decreases (Fig. 3B), while a second peak of f_{11} appears at the same position (fig. 4A).

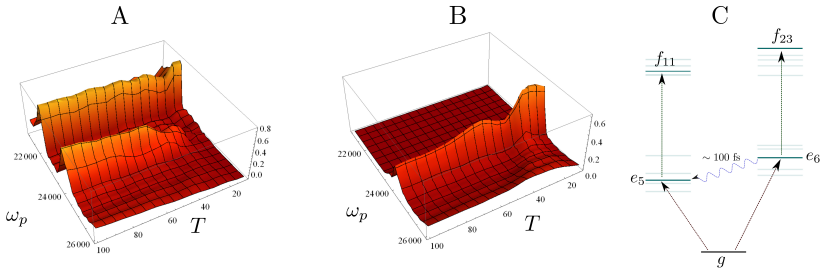

Fig. 3. The variation of the populations of the two-exciton states f_{11} (A) and f_{23} (B) with the pump frequency and the entanglement time. C: excitation pathways and population decay channel for the two states.

5 Frequency-resolved fluorescence

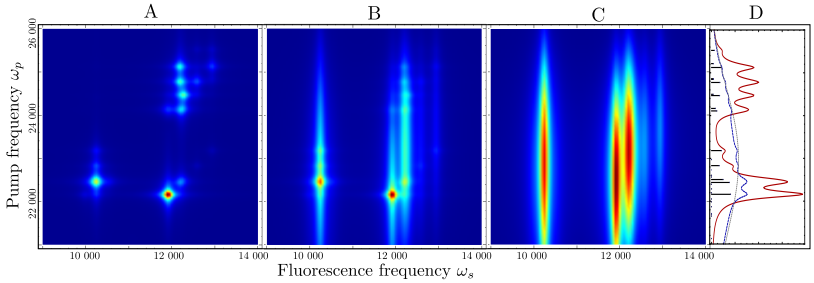

Fig. 4. The fluorescence signal induced by entangled photons (A), chirped pulses (B), and stochastic light (C). D: The fluorescence action spectrum of entangled photons (solid line), chirped pulses (dashed), and stochastic light (dotted).

The frequency-resolved $f \rightarrow e$ fluorescence signal of the double-exciton manifold corresponding to the populations of fig. 2 is shown in fig. 4. The total intensity of the signal created by entangled photons as well the relative contribution of each state can be strongly manipulated by the input light parameters (see Fig. 4A & D). As we vary ω_p, we can control different transitions (Fig. 4A). The action spectrum peaks whenever ω_p is on resonance with a double-exciton energy, highlighting the fact that the photon pair acts as a single quantum mechanical object. This behavior cannot be achieved with classical light.

6 Acknowledgements

We gratefully acknowledge the support of the National Science Foundation through Grant No. CHE-1058791, the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy, and the National Institute of Health Grant GM-59230. B. P. F. gratefully acknowledges support from the Alexander-von-Humboldt Foundation through the Feodor-Lynen program.

References

1. J. Javanainen and P.L. Gould, Phys. Rev. A **41**, 5088, (1990)
2. F. Schlawin, K. E. Dorfman, B. P. Fingerhut and S. Mukamel, arXiv: 1204.4490v1 [quant-ph], (2012)
3. B.F. Fingerhut and S. Mukamel, J. Phys. Chem. Lett., DOI: 10.1021/jz3006282, (2012)