Coherent control of the efficiency of an artificial light-harvesting complex

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Abstract. Coherent control over the branching ratio between competing pathways for energy flow is realised for artificial light-harvesting complex. Direct insights to the mechanism featuring quantum interference of a low-frequency mode are presented.

Introduction

Conversion of light energy into chemical potentials using artificial photosynthesis is an important challenge of science and technology today [1]. Nature has inspired systems based upon complicated natural light-harvesting complexes (LHCs) reduced to their basic elements [2]. In this contribution we perform Quantum Control Spectroscopy (QCS) on a dyad molecule that closely mimics the early-time photophysics of the LH2 photosynthetic antenna complex [3]. The system we study is inspired by the LH2 complex from the purple bacterium *Rhodopseudomonas acidophila* and consists of a single donor (carotenoid) and single acceptor (purpurin) moiety thus reducing the structural complexity significantly compared to the LH2. In order to control the pathways of energy flow in the dyad molecule we use femtosecond pulse shaping in a adaptive learning loop [4]. We extract recognisable features from the resulting pulse shapes, simplify the parameter space accordingly. This strategy provides a powerful spectroscopic tool that is sensitive to the function of the artificial LHC, thereby revealing important characteristics affecting the efficiency of the lightharvesting process. Furthermore, we show that it is possible to enhance or suppress the functional channel by pulse shapes exploiting different control mechanisms [5]. Ultimately, this approach may lead to the discovery of new design principles to aid the development of more efficient artificial light-harvesting systems.

Experimental Methods

The control measurements were made with a transient absorption setup using tailored pump pulse and an unmodulated probe pulse. An amplified fs laser system (Clark CPA2001), non-collinear optical parametric amplifier (NOPA), and a pulse shaper introduced into the beam path provided the pump pulses. In the pulse shaper a 640-pixel liquid-crystal spatial light modulator (SLM; Cambridge Research Instruments) is placed in the Fourier plane of a 4-f zero-dispersion compressor. Only phase shaping is used.

A robust calibration method, where each SLM pixel is calibrated and correction for any phase distortion is made by optimising second-harmonic generation in a non-linear crystal, ensured that the shaping introduced no effect on the amplitude of the pump pulse.

Results and Discussion

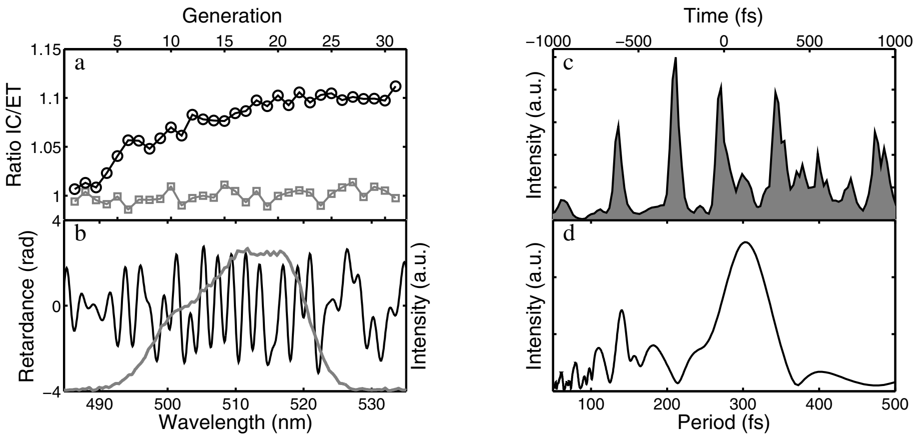

Fig. 1. Optimisation of the ratio IC/ET. (a) The learning curve shows an improvement of 10% in the fitness value of the best pulses of each generation (black circles), and the fitness of the TL pulse (grey squares), measured prior to each new generation. The initial increase of the fitness value (from TL to the first generation) due to the stretching of the pulse is subtracted from the data. (b) Pump spectrum (grey line); best found phase shape (black line). (c) Best found pulse shape. (d) FFT of the cross-correlation of the best pulse.

Fig. 1(a) shows a learning curve of an optimisation in which the target was to maximise the ratio between the two competing energy flow pathways of the dyad, internal conversion and energy transfer (IC/ET). A total of 10% increase of the ratio is obtained in the fitness values of the best pulse shapes (circles) after 31 generations. The fitness value of the transform limited (TL) pulse (squares) was determined prior to each new generation, providing an excellent indicator that the experimental conditions remained constant during the optimisation. The best found phase shape and the used pump pulse spectrum are plotted in Fig. 1(b) and the cross-correlation with an unshaped pulse in Fig. 1(c). Fig. 1(d) shows the power spectrum of the measured cross-correlation signal. Similarly, we explored a target objective aimed to improve the relative yield of the energy transfer, using fitness function ET/IC [5]. As in the case of the IC/ET optimisation, a multi-pulse structure with varying time separation between the pulses is resolved. The four-pulse structure has a total duration that is significantly shorter than the best pulse from the IC/ET optimisation, and the most pronounced sub-pulse spacing is approximately 200 fs.

The experiments show that both product channels (ET and IC) in the artificial LHC are susceptible to coherent control. Using the strategy of sequentially moving from blind optimisations to a restricted parameter space and analysing the optimisations using Fourier analysis, we find that for both product channels a pulsetrain structure with varying subpulse spacings (~300 fs for IC and ~200 fs for ET) is responsible for the control. We propose a mechanism that incorporates impulsive stimulated Raman scattering (ISRS) of low-frequency skeletal modes in the ground state. Wavepacket generation on specific vibrational modes by shaped pulses, which turns into enhancement of vibrational coherence under near-electronic resonant condition, has been demonstrated in various molecules including carotenoids. By periodically modulating the phase of the laser pulse over its spectrum, it is possible to prepare wave packets selectively and, under near-resonant conditions, to enhance wave-packet excitation of Raman-active modes. The leading pulses prepare a wave packet in the vibrationally hot ground state of the carotenoid. By matching the frequency of the pulse train to a ground-state vibrational mode (e.g., a low-frequency twisting of the backbone), we introduce momentum along a trajectory that may take the wave packet toward Franck-Condon regions not accessed by a Fourier-limited pulse. Subsequently, this push leads to an altered evolution on the excited state, either toward or away from the conical intersection between S_2 and S_1. In the former case, an excitation of vibrationally hot ground state modes could lead to a more efficient IC process, averting the ET pathway.

Conclusions

The experiments show that both product channels (ET and IC) in the artificial LHC are susceptible to coherent control. Using the strategy of sequentially moving from blind optimisations to a restricted parameter space and analysing the optimisations using Fourier analysis we find that for both product channels, a pulse train structure with varying sup-pulse spacings (around 300 fs for IC and 200 fs for ET) is responsible for the control. Thus, we have found important directions on the fitness landscape describing a smaller search space still containing the optimal solution. Many repeated runs of the recorded phase shapes from the optimisations were performed indicating that the results are repeatable and robust. The efficiency of ET in the dyad depends strongly on the photophysics of the carotenoid moiety. By reducing the parameter space in combination with the Fourier analysis of obtained pulse shapes we were able to track down the functionally important features of this molecular system. A mechanism based on the periodic excitation pulse enhancing the vibrational coherence of low-frequency wavepackets via ISRS process is most likely responsible for the control, analogous to that proposed earlier for LH2 [6].

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