Coherent Control of the Exciton Dynamics in the FMO Protein

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Abstract. We have achieved first steps toward coherent control of excitonic energy migration in the FMO pigment-protein complex, by combining femtosecond pulse shaping with a feedback loop using an evolutionary algorithm. The experimental conditions achieved, with a rotating sample, a cryostat, and a pulse shaper, are sufficient for closed loop optimizations.

Introduction

In 1975 Roger Fenna and Brian Matthews solved the X-ray structure of the water soluble bacteriochlorophyll a (BChla) protein [1]. It was isolated a decade before from green sulfur bacteria by John Olson, hence the name the Fenna-Matthews-Olson (FMO) protein [2]. The protein complex is a trimer with three identical subunits, each consisting of seven BChla pigments surrounded by a protein shell. Within green sulfur bacteria the complex is part of the photosynthetic pathway and takes care of the transfer of energy from the light-harvesting antenna to the reaction center. Since the crystal structure of the FMO complex was the first of the photosynthetic proteins to be resolved, it has been explored by a wide range of spectroscopic studies. One of which, 2D electronic spectroscopy performed by Brixner et al., revealed directly the coupling between the exciton levels [3]. Combination of the results of experiments with simulations linked the spectroscopic properties with the structure of the system.

Experimental Methods

The seven BChla pigments in the FMO protein give rise to seven excitonically coupled states. The resulting low temperature transient absorption spectrum (77K) shows three distinct peaks at 805, 815 and 825 nm respectively. These “exciton peaks” show up in the transient spectra obtained by pump-probe spectroscopy and change in time representing the energy decay along the seven exciton levels. Our aim is to influence the pathway of energy decay in this system by using coherent control. This technique uses shaped broadband laser pulses to steer a quantum system into a desired direction. The “optimal” pulse for this preset output state is often obtained in a closed loop experiment (fig.1.). In these experiments a signal representing the

desired target state is used as a feedback signal, which is optimized by an evolutionary algorithm [4].

Coherent control of excitonic wavepackets has been demonstrated before in biological systems both by experiments [5] and by computational studies [6]. We try to apply this to the FMO complex by monitoring the exciton decay by pump-probe spectroscopy and shaping the pump pulse.

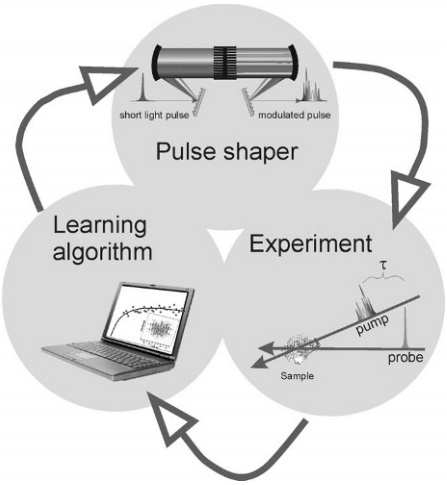

Fig. 1. Closed loop "blind" optimization of the highest exciton energy band in the FMO complex at 805 nm using phase only shaping. Feedback signals are derived from the 77K transient absorption spectrum.

Results and Discussion

The excitation energy in the FMO complex decays downwards starting from the state at 805 nm within ~10 ps. As a target we chose to optimize the intensity of the band at 805 nm at 3 ps delay. The pulse shaper in our experiment (CRi SLM-640) is capable of shifting the pulse in time by ± 6 ps simply by adding a linear chirp. To prevent the trivial solution of the arrival of the pump pulse 3 ps later we therefore restricted the linear chirp to have zero slope, in order to fix the center of mass in the time domain around t_0. The resulting optimal pulse shape of the optimization still partly shows the trivial solution of a peak at 3 ps (fig.2.). However, there is significant additional structure to the pulse that suggests the involvement of additional processes. We are currently trying to see if the optimized pulse induces any coherent processes by comparing data and simulations of the time-dependent pump-probe spectra with the transform limited pulses and with the optimized pulses.

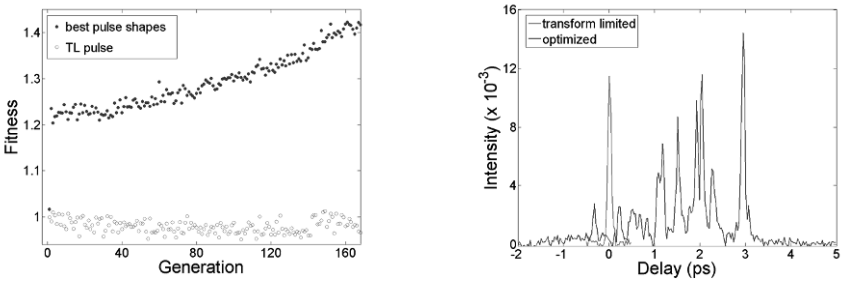

Fig. 2. [Left] Learning curve of the optimization of the 805 nm exciton band at 3 ps pump-probe delay. The monitor the laser drifting the fitness value of the TL pulse was measured before each new generation. [Right] XFROG signal showing the TL pulse (dashed line) and the optimized pulse shape (solid line) at 400 nm.

Conclusions

We have performed femtosecond pump-probe studies using transform limited and phase-shaped pulses in an attempt to manipulate the pathway of excitonic energy migration within the FMO complex. While the learning curve is complicated due to an underlying trivial control effect, the resulting complex pulse shapes suggest a mechanism involving low-frequency vibrational modes. Further experiments combined with simulations are needed to fully understand this effect.

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