Coherence in Oxygenic Photosynthesis

Franklin D. Fuller[1], Jie Pan[1], Andrius Gelzinis[2,3], Vytautas Butkus[2,3], S. Seckin Senlik[1], Daniel E. Wilcox[1], Leonas Valkunas[2,3], Darius Abramavicius[2] and Jennifer P. Ogilvie[1]

[1]Department of Physics and Biophysics, University of Michigan, Ann Arbor, MI 48109

[2]Department of Theoretical Physics, Faculty of Physics of Vilnius University, Sauletekio Avenue 9, Building 3, 10222 Vilnius, Lithuania

[3]Center for Physical Sciences and Technology, Gostauto 9, 01108 Vilnius, Lithuania

jogilvie@umich.edu

Abstract: We report coherent dynamics in the photosystem II reaction center observed by two dimensional electronic spectroscopy. We discuss the physical nature of the coherences and their importance for charge separation.

OCIS codes: (300.6530); (300.6300); (300.6290)

1. Introduction

Photosynthetic systems contain light-harvesting antennae arrays that gather solar energy and transfer it to reaction centers where it is converted to a charge separated state. In oxygenic photosynthesis the first charge separation event occurs in the Photosystem II reaction center (PSII RC); the only natural biological system capable of using solar energy to split water. Two-dimensional electronic spectroscopy (2DES) has provided an incisive tool for studying energy transfer and the electronic structure of photosynthetic complexes [1]. 2DES provides a direct view of populations and coherences that appear on the diagonal and off-diagonal regions of a 2D spectrum. 2DES studies of a number of photosynthetic systems have revealed coherent oscillations as a function of population time [2-4]. An intense ongoing debate aims to understand the physical nature of the coherences and their possible role in enhancing energy transfer. While the bulk of 2DES experiments have focused on light harvesting antenna, 2DES has recently been applied to reaction centers [5, 6]. Here we report clear coherent signatures in the 2DES spectra of the PSII RC. We also discuss the physical origins of the coherences and speculate about their relevance to the essential charge separation function in the PSII RC.

2. Methods

D1-D2-cyt *b*559 reaction centers were isolated as described previously [5]. Glycerol was added to produce a glycerol:buffer ratio of 2:1 (v/v), and the sample was vacuum degassed prior to being sealed in an optical cell with a sample thickness of 380 μm and an OD of ~0.2 at 680 nm. The 2DES measurements were made using a hybrid diffractive optic and pulse-shaping based approach that combines the advantages of background-free detection with the precise time-delays and phase-cycling capabilities of a pulse-shaper [7]. The 2DES spectra were phased to pump probe data using the projection slice theorem [8]. In order to resolve low frequency modes, population kinetics were removed using a global exponential fit.

3. Results

Figure 1 shows a typical absorptive 2DES spectrum of the PSII RC at a population time of 170 fs. Marked on the spectrum (arrows) are several diagonal and off-diagonal locations where we observe strong coherences as a function of the population time (t_2). The frequency content of these individual time traces is also shown in Figure 1, where the Fourier transform has been taken with respect to t_2 after removal of background kinetics. We observe dominant coherences at 91 cm^{-1}, 127 cm^{-1}, 251 cm^{-1}, 339 cm^{-1}, 730 cm^{-1}, 854 cm^{-1} and 974 cm^{-1}. Electronic coherence between excitonic states should manifest itself as modulation in the off-diagonal 2D spectrum region as a function of t_2. This modulation should occur at a frequency that corresponds to the difference frequency between the participating excitonic states[2]. We find that the lowest four observed modes closely match exciton difference frequencies within the Novoderezhkin [9] and Gelzinis [10] models. All but the 127 cm^{-1} mode also reasonably match vibrational frequencies as determined by Raman [11] or fluorescence line-narrowing [12] experiments.

The coherences we observe here persist on picosecond timescales at 77 K. In both the BRC and the PSII RC this time scale is coincident with the primary charge separation steps, raising the interesting question of whether the coherent dynamics are important for the charge separation process. To understand the origin of the experimentally observed coherences and determine their importance for charge separation, we have performed theoretical simulations of the dimeric special pair of the PSII RC including explicit coupling to discrete vibrations, using an approach recently developed by Butkus et al. [13]. The simulations show that molecular vibrations strongly modulate the 2D spectra, and that coupling the special pair electronic dimer to a single vibrational mode creates

coherences at several frequencies. Additional simulations find that particular vibrations observed by 2DES dramatically speed up the rate of initial charge separation in the PSII RC.

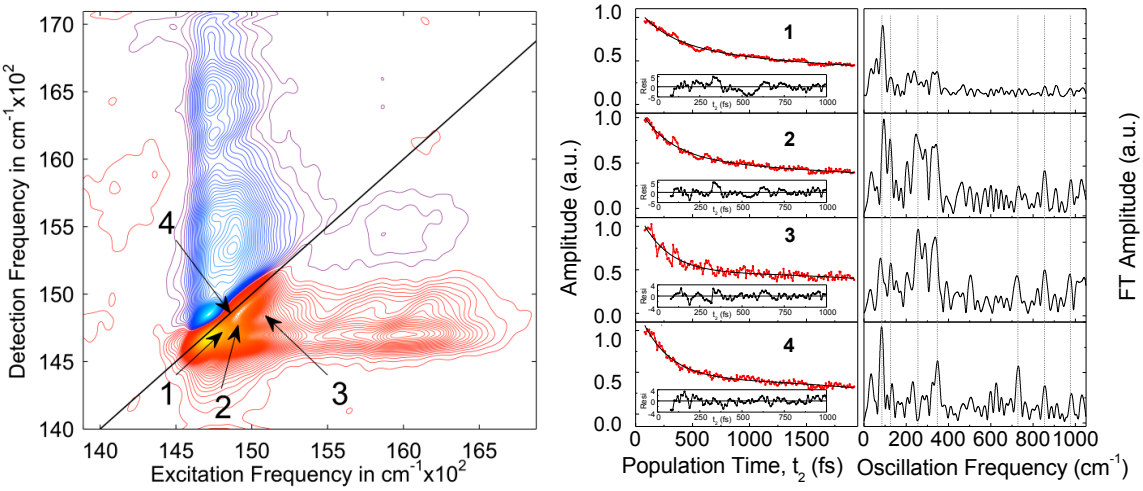

Figure 1. Left: Absorptive (real, phased) 2D spectrum of the PSII RC at 77K at a population time of 170 fs. Right: Representative population time (t_2) traces taken at the locations indicated by the numbered arrows. Data is shown in red, with background fit in black. The insets show the data after subtraction of the background. Also shown are the corresponding Fourier transforms of the population time traces (taken after background subtraction). Gray vertical lines show locations of peaks found consistently throughout the 2D spectrum.

4. References

1. T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship, and G. R. Fleming, "Two-dimensional spectroscopy of electronic couplings in photosynthesis," Nature **434**, 625-628 (2005).
2. G. S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn, T. Mancal, Y. C. Cheng, R. E. Blankenship, and G. R. Fleming, "Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems," Nature **446**, 782-786 (2007).
3. D. B. Turner, R. Dinshaw, K. K. Lee, M. S. Belsley, K. E. Wilk, P. M. G. Curmi, and G. D. Scholes, "Quantitative investigations of quantum coherence for a light-harvesting protein at conditions simulating photosynthesis," Physical Chemistry Chemical Physics **14**, 4857-4874 (2012).
4. J. M. Womick and A. M. Moran, "Exciton Coherence and Energy Transport in the Light-Harvesting Dimers of Allophycocyanin," Journal of Physical Chemistry B **113**, 15747-15759 (2009).
5. J. A. Myers, K. L. M. Lewis, F. D. Fuller, P. F. Tekavec, C. F. Yocum, and J. P. Ogilvie, "Two-dimensional electronic spectroscopy of the D1-D2-cyt b559 photosystem II reaction center complex," Journal of Physical Chemistry Letters **1**, 2774-2780 (2010).
6. S. Westenhoff, D. Palecek, P. Edlund, P. Smith, and D. Zigmantas, "Coherent Picosecond Exciton Dynamics in a Photosynthetic Reaction Center," Journal of the American Chemical Society **134**, 16484-16487 (2012).
7. F. D. Fuller, D. E. Wilcox, and J. P. Ogilvie, "Pulse shaping based two-dimensional electronic spectroscopy in a background free geometry," Optics Express **22**, 1018-1027 (2014).
8. J. D. Hybl, A. A. Ferro, and D. M. Jonas, "Two-dimensional Fourier transform electronic spectroscopy," Journal Of Chemical Physics **115**, 6606-6622 (2001).
9. V. I. Novoderezhkin, J. P. Dekker, and R. van Grondelle, "Mixing of exciton and charge-transfer states in Photosystem II reaction centers: Modeling of Stark spectra with modified Redfield theory," Biophysical Journal **93**, 1293-1311 (2007).
10. A. Gelzinis, F. D. Fuller, L. Valkunas, J. P. Ogilvie, S. Mukamel, and D. Abramavicius, "Tight-binding model of the photosystem II reaction center: application to two-dimensional spectroscopy," New Journal of Physics **15**, 075013 (2013).
11. R. Picorel, G. Chumanov, E. Torrado, T. M. Cotton, and M. Seibert, "Surface-enhanced resonance Raman scattering spectroscopy of plant photosystem II reaction centers excited on the red-edge of the Q(y) band," Journal of Physical Chemistry B **102**, 2609-2613 (1998).
12. E. J. G. Peterman, H. van Amerongen, R. van Grondelle, and J. P. Dekker, "The nature of the excited state of the reaction center of photosystem II of green plants: A high-resolution fluorescence spectroscopy study," Proceedings of the National Academy of Sciences of the United States of America **95**, 6128-6133 (1998).
13. V. Butkus, D. Zigmantas, D. Abramavicius, and L. Valkunas, "Distinctive character of electronic and vibrational coherences in disordered molecular aggregates," Chemical Physics Letters **587**, 93-98 (2013).