

Final Technical Report: DE-FG02-07ER15904
Two-Dimensional Electronic Spectroscopies for Probing Electronic Structure and Charge Transfer: Applications to Photosystem II

Overall research goals:

Photosystem II (PSII) is the only known natural enzyme that uses solar energy to split water, making the elucidation of its design principles critical for our fundamental understanding of photosynthesis and for our ability to mimic PSII's remarkable properties. This project focuses on key deficits in our current understanding of the PSII reaction center (PSII RC). The project involves the development of new spectroscopic methods, and their application to address the following open questions:

- 1) What is the electronic structure of the PSII RC?
- 2) What are the charge separation pathways in the PSII RC?
- 3) Does coherence facilitate charge separation in the PSII RC?

Over the course of this grant period we have continued our development of new multidimensional spectroscopy methods, and have used the new methods to study the photosystem II reaction center (PSII RC) using D1-D2-cytb559 preparations as well as PSII "core" complexes (which include additional antennae CP43 and CP47). We have also performed several studies of Chlorophyll a (Chl a) to facilitate our understanding of the spectroscopy of the larger PSII RC system. We are collaborating with the theory group of Darius Abramavicius to enable a combined experimental-theoretical approach to address the three open questions stated above. We have published several papers during this grant period¹⁻⁶ and have several papers submitted⁷⁻⁸ and others in progress⁹⁻¹⁰.

Vibronic Coherence in the PSII RC⁴:

We have developed a novel implementation of 2DES that built on our previous work and provided ~20-fold enhancement in signal-to-noise ratio³. Upon using our improved 2DES implementation to study the PSII RC, our data clearly revealed the presence of coherent dynamics. There is currently considerable debate in the field about the physical origin of coherent dynamics and their potential importance for photosynthetic function. Supported by simulation work and extensive characterization of the coherences we believe that they have mixed electronic and vibrational character and that they are functionally importance for charge separation. To assign the origin of the experimentally observed coherences and determine their influence on charge separation, we performed theoretical simulations of the dimeric special pair of the PSII RC including explicit coupling to discrete vibrations, obtaining good agreement with the experimental data, as shown in Figure 1. Further simulations using an exact hierarchical equations of motion (HEOM) method demonstrated that resonant vibrations speed up the initial step of charge separation in the PSII RC. This is shown in Figure 1, where we consider the effect of one of the observed vibronic coherences on the charge transfer (CT) state population evolution. Here we consider the 339 cm⁻¹ vibronic coherence and compare the *coherent* (weakly damped) and *incoherent* (strongly damped) cases. These cases correspond to different protein spectral densities as shown in the inset in Figure 1. We see that the coherent 339 cm⁻¹ vibration dramatically increases the growth of the CT state population compared to the damped case. With the exception of the 251 cm⁻¹ vibration, the other vibrational frequencies affect the CT state population weakly. The origin of the CT enhancement effect is related to the

optical excitonic splittings: when the vibrational frequency is close to excitonic resonance, the vibrational coherence effectively drives the charge separation. Such vibrational/excitonic resonance also results in the speed-up of energy relaxation, i.e., exciton transport or charge separation. *This may represent an important design principle for enabling the high quantum efficiency of charge separation in oxygenic photosynthesis.* In the next funding period we aim to further examine both the physical origin of the observed coherences and their importance for charge separation. We published this work in Nature Chemistry ⁴.

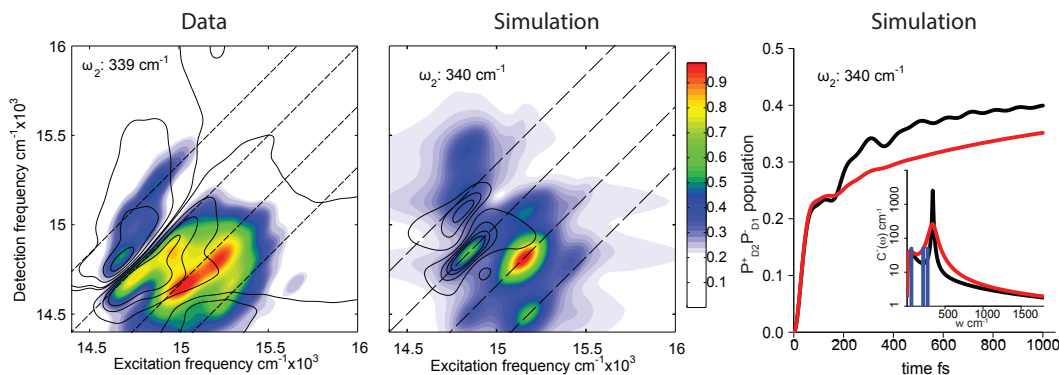


Figure 1: Left: Coherence amplitude map (filled contours) derived from the real rephasing 2D spectra at $\omega_2 = 339 \text{ cm}^{-1}$. These maps show the distribution of observed coherences throughout the entire 2D spectrum. Middle: Simulated coherence amplitude maps (filled contours) derived from the simulated real rephasing 2D spectra for the special pair dimer model with a 339 cm^{-1} mode, showing good agreement between theory and experiment. The dashed black lines indicate the diagonal and parallel lines offset from the diagonal by $\pm\omega_2$ and $-2\omega_2$. Overlaid open contours show the real rephasing 2D spectrum, averaged over waiting time t_2 . Right: Simulated population of the charge transfer state for coherent and incoherent cases of the 340 cm^{-1} vibrational mode. The bath spectral densities for the coherent (black line) and incoherent (red line) mode are shown in the inset. Blue lines mark optical excitonic splittings.

Energy transfer in PSII core complexes⁷:

Our previous 2DES experiments have been performed on the D1D2 cyt-b559 complex. Concerns that this complex may have a perturbed excitonic structure motivated us to study PSII core complexes that consist of the intact PSII RC complex (with quinones) and the neighboring antenna complexes CP43 and CP47. We have performed polarization-dependent 2DES studies of the PSII core preparation at 77K, shown in Figure 1. Despite the predicted small electronic coupling in this system, we see extremely rapid energy transfer within the first 100 fs, as shown by the cross-peak features in the parallel and perpendicular 2D spectra at the earliest waiting time delays. We have simulated the early energy transfer events using two different approaches. The first approach considers evolution of only the electronic energy in the system and fails to reproduce the ultrafast energy transfer dynamics. A second approach that considers the combined dynamics of both electronic and vibrational degrees of freedom reproduces the observed sub-100 fs evolution. This implies that vibrational degrees of freedom not only induce population transfer between the excitonic states in the PSII CC, but also shape the energy landscape of the system.

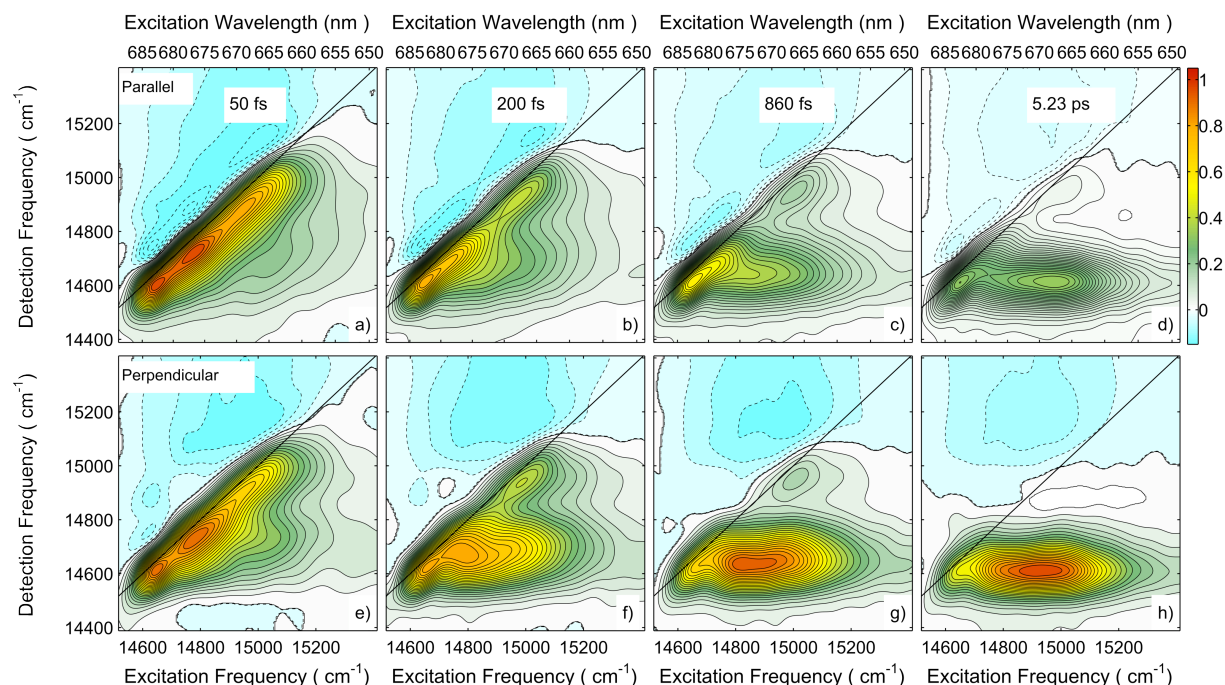


Figure 2: 2D Electronic Spectra of the PSII core complexes at 77K recorded at different t_2 waiting times as labeled. Upper panels, all pump and probe pulses are parallel (a-d); Bottom panels, the polarization of two pump pulses was perpendicular to that of the probe pulse (e-h). In both polarization conditions, spectral amplitudes are normalized to the maximum of the earliest t_2 time spectrum after pulse overlap coherent effects are largely complete. Positive amplitude is shown in solid contour lines, and negative amplitude in dashed lines.

Two-color nonlinear spectroscopy for the rapid acquisition of coherent dynamics¹:

There has been considerable recent interest in the observation of coherent dynamics in photosynthetic systems by 2DES. In particular, coherences that persist during the “waiting time” in a 2DES experiment have been attributed to electronic, vibrational and vibronic origins in various systems. The typical method for characterizing these coherent dynamics requires the acquisition of 2DES spectra as a function of waiting time; essentially a 3DES measurement. Such experiments require lengthy data acquisition times that degrade the signal-to-noise of the recorded coherent dynamics. We have developed a rapid and high signal-to-noise pulse-shaping-based approach for the characterization of coherent dynamics, which we call two-color rapid acquisition coherence spectroscopy (T-RACS). We have demonstrated that the method retains much of the information content of a 3DES measurement and have used it to study Chlorophyll a (Chl a). Understanding the coherent dynamics in Chl a is an important step towards better understanding the more complex dynamics of the PSII RC. We have shown that the T-RACS approach can distinguish between ground and excited state coherence, an important feature that will assist us in our studies of the functional importance of the observed coherences.

Is coherence important for charge separation⁹?

Our Nature Chemistry paper reported vibronic coherence in the PSII RC in the Q_y region. If indeed the coherence is important for charge separation, it should modulate the formation of the charge separated state. Aided by the improved signal-to-noise ratio of the T-RACS approach, we have detected coherence in the anion band of the PSII RC.

This is an ongoing study but at this point our observations strongly support the importance of the coherence for charge separation.

2D electronic Stark spectroscopy (2DESS)⁸:

Characterizing ultrafast energy and charge transfer is important for our understanding of a wide range of systems, from the PSII RC to organic photovoltaics. Distinguishing the kinetic processes of energy transfer and charge separation in such systems is challenging due to the lack of clear spectral signatures of charge transfer states, which are typically non-radiative. Linear Stark spectroscopy has proven to be a valuable method for uncovering charge transfer states in photosynthetic reaction centers. Pump-probe spectroscopy in the presence of strong external electric fields has been used to study the kinetics of charge transfer and recombination in biological and organic semiconductor systems. The magnitude of the electric-field-dependent kinetics is often small, necessitating a sensitive spectroscopic method. We have developed a heterodyne-detected multidimensional Stark spectroscopy method for observing CT dynamics with increased sensitivity and temporal-resolution. These measurements require that high electric fields be applied to the sample, while maintaining the appropriate optical density (~ 0.3) for high signal-to-noise experiments. This is challenging because the pathlength must remain small (~ 50 microns) to achieve the requisite fields. We first applied the 2DESS method to study TIPS-pentacene, and a methods paper is currently under review.⁸ We have also successfully applied 2DESS to studies of the D1D2-RC, and show representative data in Figure 3. Although it is well-known that in the PSII RC the final charge-separation is mediated by a series of charge-transfer intermediates, the detailed mechanism remains open to debate. In particular, there is evidence that there are multiple pathways that lead to the final charge-separated state that differ in the identity of the primary radical pair. A major difficulty in differentiating between proposed kinetic models is spectral overlap of the pigments participating in the reaction and the elusive nature of the charge-transfer states. Our 2DESS technique preferentially enhances the ability to detect these charge transfer states and their coupling to excitonic states. The data shown in Figure 3 shows distinct spectral features at wavelengths that are in reasonable agreement with proposed charge transfer states of the PSII RC. The 2DESS technique should be widely applicable to the study of ultrafast charge-transfer processes in a broad range of systems.

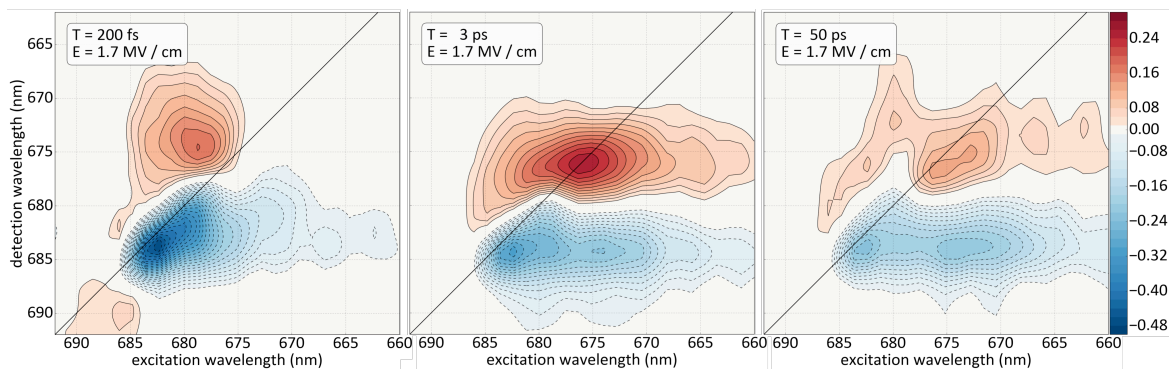


Figure 3: 2DESS spectra with an applied Stark field of 1.7 MV/cm at different population times $T=200$ fs, 3 ps and 50 ps (left to right). Three percent thresholding was applied to the spectra.

Improving excitonic models of the PSII RC:

A wealth of ultrafast spectroscopic studies have aimed at understanding the PSII RC. One of the greatest challenges in understanding the energy and charge transfer events in the PSII RC is that it contains many chromophores with overlapping electronic transitions, making the interpretation of time-resolved spectroscopic data difficult. Transient absorption studies have aimed to selectively excite portions of the spectra. However, in transient absorption studies excitation selectivity comes at the expense of time resolution. In contrast, 2DES is well-suited to studying congested spectra; it resolves both the excitation and detection frequency with simultaneously high time and frequency resolution, allowing for better discrimination between overlapping signals. We have previously used our 2DES data to test current excitonic models of the PSII RC¹¹⁻¹². We have found that the excitonic model captures some of the main features of the data but fails to describe the rapid relaxation within the first few hundred femtoseconds, and poorly describes the subsequent kinetics due to charge separation. We are continuing collaborations with Shaul Mukamel and Darius Abramavicius towards simulating 2DES spectra. Based on the excitonic models we have developed in our 2DES studies we are now combining these models with explicit charge transfer states and will use our 2DESS data to test the new models¹⁰. We expect that the improved ability to monitor the charge separation process with 2DESS will prove useful for distinguishing between recently-proposed charge separation models. We will also be able to use this model to better understand the role of particular vibrations in aiding the charge separation process in the PSII RC.

1. Senlik, S.; Policht, V.; Ogilvie, J. P. Two-Color Nonlinear Spectroscopy for the Rapid Acquisition of Coherent Dynamics. *Journal of Physical Chemistry Letters* **2015**, *6*, 2413-2420.
2. Fuller, F. D.; Ogilvie, J. P. Experimental Implementations of 2D Fourier Transform Electronic Spectroscopy. *Annual Reviews of Physical Chemistry* **2015**, *66*, 667-690.
3. Fuller, F. D.; Wilcox, D. E.; Ogilvie, J. P. Pulse Shaping Based Two-dimensional Electronic Spectroscopy in a Background Free Geometry. *Optics Express* **2014**, *22*, 1018-1027.
4. Fuller, F. D.; Pan, J.; Butkus, V.; Gelzinis, A.; Senlik, S.; Wilcox, D. E.; Yocum, C. F.; Valkunas, L.; Abramavicius, D.; Ogilvie, J. P. Vibronic Coherence in Oxygenic Photosynthesis. *Nature Chemistry* **2014**, *6*, 706-711.
5. Loukianov, A.; Niedringhaus, A.; Pan, J.; Ogilvie, J. P. 2D Electronic Stark Spectroscopy. *Xvth International Conference on Ultrafast Phenomena* **2016**, in press.
6. Fuller, F. D.; Pan, J.; Gelzinis, A.; Butkus, V.; Senlik, S. S.; Wilcox, D. E.; Valkunas, L.; Abramavicius, D.; Ogilvie, J. P. Coherence in Oxygenic Photosynthesis. *Xivth International Conference on Ultrafast Phenomena* **2014**, *42*, in press.
7. Pan, J.; Gelzinis, A.; Senlik, S.; Valkunas, L.; Abramavicius, D.; Ogilvie, J. P. Two-dimensional electronic spectroscopy of the Photosystem II core complex. *submitted* **2016**.
8. Loukianov, A.; Niedringhaus, A.; Berg, B.; Pan, J.; Senlik, S.; Ogilvie, J. P. Two-dimensional electronic Stark spectroscopy *submitted* **2016**.

9. Senlik, S.; Loukianov, A.; Policht, V. Observation of coherent dynamics in the charge separated state of the photosystem II reaction center. *in preparation* **2016**.
10. Loukianov, A.; Niedringhaus, A.; Senlik, S.; Pan, J.; Berg, B.; Ogilvie, J. P. Two dimensional electronic Stark spectroscopy of charge separation in the photosystem II reaction center. *in preparation* **2016**.
11. Lewis, K. L. M.; Fuller, F. D.; Myers, J. A.; Yocum, C. F.; Mukamel, S.; Abramavicius, D.; Ogilvie, J. P. Simulations of the Two-Dimensional Electronic Spectroscopy of the Photosystem II Reaction Center. *Journal of Physical Chemistry A* **2013**, *117*, 34-41.
12. Gelzinis, A.; Valkunas, L.; Fuller, F. D.; Ogilvie, J. P.; Mukamel, S.; Abramavicius, D. Tight-binding model of the photosystem II reaction center: application to two-dimensional electronic spectroscopy. *New Journal of Physics* **2013**, *15*, 075013.