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Probing quantum coherence in bacterial photosynthesis at the ensemble and single complex level

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14. ABSTRACT

This project developed novel experimental spectroscopy and imaging approaches, at and below the diffraction limit, to enable the elucidation of quantum effects in biological systems. Using purple sulfur photosynthetic bacteria as a model system, we aimed to understand the physical origin of recently observed quantum coherence in photosynthetic antennae complexes and to determine its importance for efficient energy transfer. Fluorescencebased two dimensional electronic spectroscopy (F-2DES) was developed to extensively characterize coherent dynamics at the ensemble and single photosynthetic complex level. F-2DES was shown to be a highly sensitive method for distinguishing between vibrational, electronic and vibronic coherence. Combined with confocal microscopy, the approach was used to resolve excitonic structure in live colonies of purple bacteria, and coherence in vivo. With an understanding of the key design elements of biological systems that exploit quantum effects to optimize their function, it may be possible to mimic such design principles in artificial materials for energy capture, conversion and human use. The proposed research supports technological advances in application areas of interest to the United States Air Force.

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Final report: Probing Quantum Coherence in Bacterial Photosynthesis at the Ensemble and Single Complex Level

Project Summary: This project aimed to develop novel experimental spectroscopy and imaging approaches, at and below the diffraction limit, to enable the elucidation of quantum effects in biological systems. Using purple sulfur photosynthetic bacteria as a model system, we aimed to understand the physical origin of recently observed quantum coherence in photosynthetic antennae complexes and to determine its importance for efficient energy transfer. The project developed a novel implementation of multidimensional spectroscopy employing fluorescence-based to enable enhanced sensitivity and spatially resolved measurements. We successfully developed the approach and achieved the following goals:

1) Demonstration of fluorescence-detected two-dimensional electronic spectroscopy for the detection of coherence in molecular systems
2) Detection of coherence in small ensembles (~2000 molecules)
3) First spatially resolved detection of the excitonic structure and ultrafast processes in purple bacterial membranes

The proposed measurements will challenge theoretical and computational approaches to capture the observed quantum and non-equilibrium phenomena. With an understanding of the key design elements of biological systems that exploit quantum effects to optimize their function, it may be possible to mimic such design principles in artificial materials for energy capture, conversion and human use. The proposed research supports technological advances in application areas of interest to the United States Air Force, including biologically inspired new innovative and novel materials, human performance and enhanced computational development for future Air force needs.

1) Demonstration of fluorescence-detected two-dimensional electronic spectroscopy for the detection of coherence in molecular systems[1, 2]

To demonstrate our fluorescence-detected two-dimensional electronic spectroscopy (F-2DES) we studied a strongly coupled symmetric bacteriochlorin dyad, a relevant ‘toy’ model for photosynthetic energy and charge transfer. Figure 1 shows the experimental setup we used, which employs phase-modulation to separate the desired signal from the collinear sequence of excitation pulses.

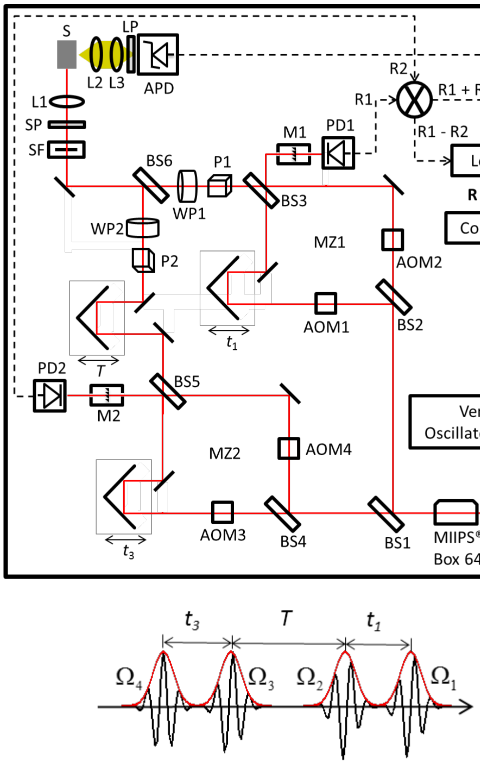

Fig. 1. Experimental setup of the F-2DES spectrometer. Beamsplitter (BS), Acousto-Optic Modulator (AOM), Mach-Zehnder interferometer (MZ), Monochromator (M), Polarizer (P), Waveplate (WP), Photodiode (PD), Spatial Filter (SF), Shortpass Optical Filter (SP), Lens (L), Sample (S), Longpass Optical Filter (LP), Avalanche Photodiode (APD), Electronic Reference Signal (R1,R2), Rephasing (**R**) and Nonrephasing (**NR**) 2D signals. The experimentally controllable carrier envelope time delays t_1, T, t_3 , between exciting pulses are shown in the lower panel.

In Figure 2 we show the molecular dyad structure and typical F-2DES spectra collected at different T values. The data shows the high signal-to-noise ratio achievable with our setup. By recording spectra as a function of T we can resolve coherent dynamics in the system.

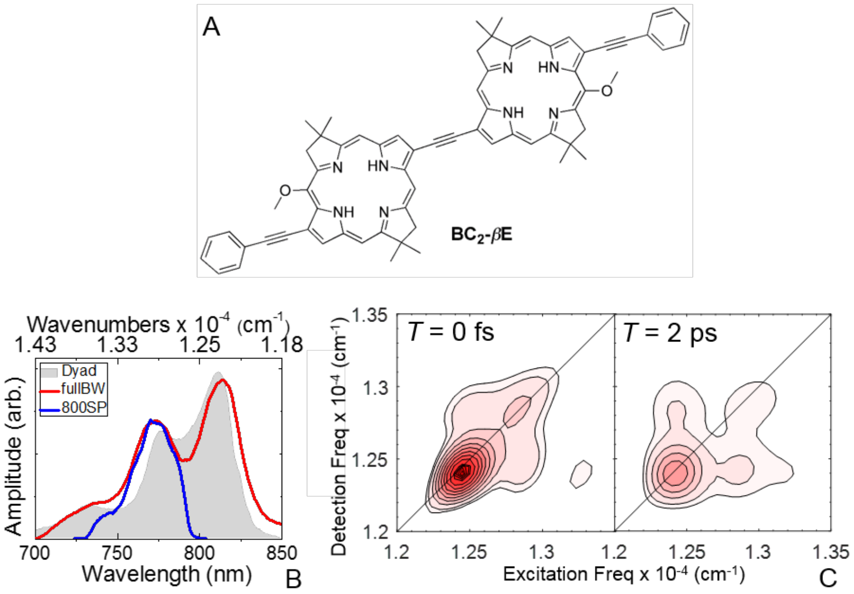

Fig. 2. (A) Chemical structure of the symmetric bacteriochlorin dyad BC$_2$βE. (B) Linear absorption spectrum of the dyad with the full laser spectrum ('fullBW'), and the laser spectrum with an 800 shortpass filter ('800SP'). (C) Absorptive F-2DES spectra at waiting time T = 0 and 2 ps, corresponding to the 'fullBW' laser spectrum. Contours are drawn at 5%,10-90%,95%,98% and 100% signal levels.

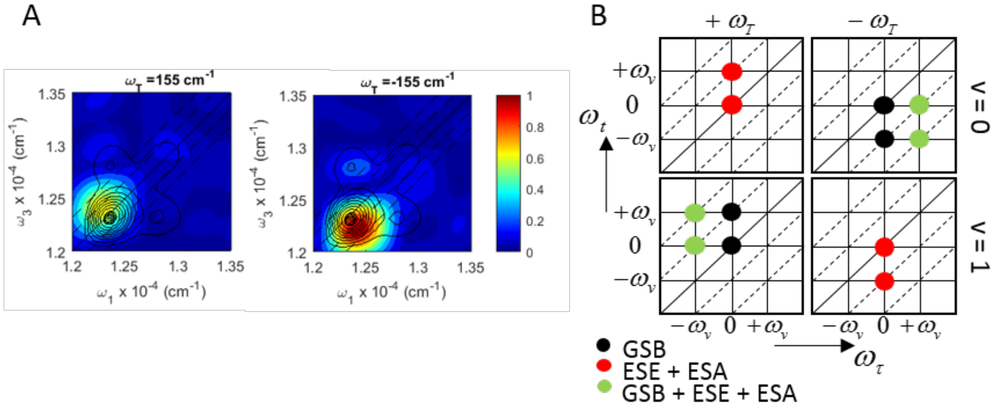

Fig. 3. (A) Absolute value rephasing coherence maps for $\omega_T = \pm 155\,\mathrm{cm}^{-1}$. The dashed line are displaced from the diagonal by ±155 cm^{-1}. Real absorptive 2D spectrum at T = 50 fs is overlaid in the background for reference. (B) Contributions to the rephasing F-2DES coherence map expected from a displaced harmonic oscillator model for an isolated pigment with one FC active vibrational mode with frequency ω_T. The model predicts purely vibrational coherences at frequency ω_T which are separable into positive and negative coherence frequencies shown in the left and right columns, respectively. The upper panels correspond to contributions for which the corresponding Feynman pathways start from the zero-point level (v = 0) on the ground state. Lower panels show contributions for which the corresponding Feynman pathways start from v = 1 vibrational level on the ground electronic state. In F-2DES, ESA signal can have positive and negative contributions. Assuming that electronic state with more than one quantum of excitation have negligible quantum

yields, the ESA signal considered in this analysis has a positive sign, similar to GSB and ESE signals.

Figure 3(A) shows 2D "coherence map" for the dominant 155 cm^{-1} frequency that was observed in the 2D data. Separation of coherent signal into positive and negative coherence frequency is routinely done in 2DES experiments in order to determine the physical origin (ground versus excited state, and purely vibrational, electronic or vibrational-electronic) of the coherent signal. The absolute value rephasing coherence maps for the most prominent coherence frequency $\omega_T = \pm 155$ cm^{-1} are shown on the same contour scale. Analysis of kinetic rate maps and coherence maps does not show any signatures of purely electronic coherence. A vibrational-electronic resonance is energetically established for the dyad, but no signatures of enhanced vibrational wavepackets at the resonant vibrational frequency were found. This may indicate that appropriate symmetry requirements for the enhancement of vibrational wavepackets are not met. It may also reflect the deviation of the dyad from a purely excitonic dimer. A picosecond transfer between the excited electronic states of the dyad and weakly underdamped low-frequency vibrational wavepackets were observed. Future F-2DES and resonance Raman experiments on bacteriochlorin monomers, and solvent dependence of the rate maps will shed more light on the reported findings.

2) Detection of coherence in small ensembles (~2000 molecules)

We have performed F-2DES measurements on the light-harvesting 2 (LH2) complex from *Rhodobacter spheroides* (see Figure 4). Also shown in Figure 4 is a coherence map for the 740 cm^{-1} mode which is resonant with the energy gap between the B800 and B850 transitions of LH2 and may be important for energy transfer efficiency in the LH2 complex. We are currently working with a theory collaborator to model our data and assess the relevance of the 740 cm^{-1} coherence to energy transfer efficiency in LH2.

We have obtained F-2DES data of similar quality for Figure 4 from only ~2000 LH2 complexes within the focal volume, an improvement of ~6 orders of magnitude over absorption-based 2D measurements. The high signal-to-noise ratio of the data suggests that we will be able to reach ~10-100 complexes without significant difficulty, enabling us to probe the true dephasing of coherence in photosynthetic systems, free from ensemble averaging. Upon optimizing the sample photostability we may be able measure F-2DES signal from a single complex. Should the sample photostability be insufficient, we will still be able to perform a lower dimensional experiment to measure coherence in single complexes. These measurements will be the first of their kind and will resolve outstanding questions about the true dephasing rate of coherence in biological systems. For example, the dephasing time of electronic, vibrational or vibronic coherence within single complexes could be considerably longer than the averaged value obtained in ensemble 2DFS measurements. Measurements on single photosynthetic complexes, or on small numbers of them offers insight into the true nature of and timescales of dephasing.

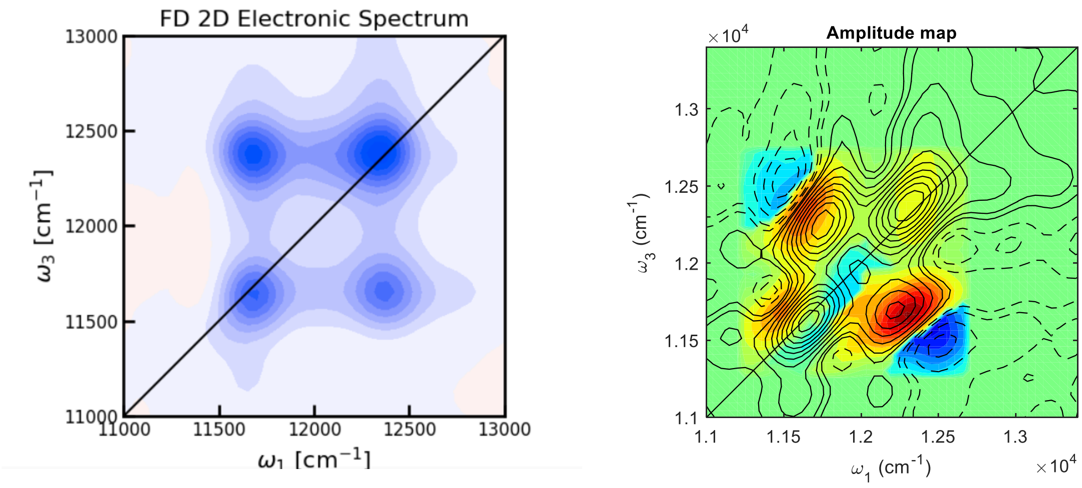

Figure 4: Left: F-2DES spectrum of ~2000 LH2 complexes, taken at a population waiting time of T= 0 fs. Right: Coherence amplitude map extracted for a 740 cm^{-1} mode resonant with the B800-B850 energy gap of LH2.

The high sensitivity of our F-2DES approach has also enabled us to make measurements on live cells as discussed below.

3) First spatially resolved detection of the excitonic structure and ultrafast processes in purple bacterial membranes[4, 5]

We have demonstrated *in vivo* spatially-resolved measurements of 2D electronic spectra from colonies of photosynthetic bacteria grown under different light intensity conditions and have resolved the resulting differences in excitonic structure of the antenna proteins inside the cells. The Coulomb couplings between electronic levels and their perturbations with growth conditions are reflected as spatial variations in the well-resolved 2D peak amplitudes that arise from spatial heterogeneity in the bacterial colonies. The fluorescence-detection approach we adopt offers significant sensitivity improvements over conventional heterodyne detection. Employing phase-modulation rather than phase-cycling enables imaging at high repetition rates, and produces spectra with a high signal-to-noise ratio without the need to combine multiple phase-cycled scans that could be susceptible to photobleaching. Our work serves as a proof-of-concept demonstration of the broad applicability of the SF-2DES approach towards resolving the connections between morphological variations, the resulting electronic couplings, and ultimately the performance of a variety of light-harvesting materials.

1. Tiwari, V.; Acosta Matutes, Y.; Yu, Z.; Ptaszek, M.; Bocian, D. F.; Holten, D.; Kirmaier, C.; Konar, A.; Ogilvie, J. P. *arXiv:1806.00896 [physics.chem-ph]* **2018**.
2. Tiwari, V.; Acosta Matutes, Y.; Yu, Z.; Ptaszek, M.; Bocian, D. F.; Holten, D.; Kirmaier, C.; Konar, A.; Ogilvie, J. P. *accepted to Optics Express* **2018**.

3. Tiwari, V.; Acosta, Y.; Ogilvie, J. P. *in preparation* **2017**.
4. Tiwari, V.; Acosta Matutes, Y.; Gardiner, A.; Cogdell, R. J.; Ogilvie, J. P. *under final review at Nature Communications* **2018**.
5. Tiwari, V.; Acosta Matutes, Y.; Gardiner, A.; Cogdell, R. J.; Ogilvie, J. P. *arXiv:1802.04395v2 [physics.chem-ph]* **2017**.