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Broadband Adjustable Repetition Rate Laser System

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This project enabled the acquisition of a broadband adjustable repetition rate laser system to enable the elucidation of quantum effects in biological systems. The project goals are to employ the adjustable repetition rate laser to enhance the PI's current research effort in three critical ways:
1) The adjustable repetition rate of the proposed laser source will enable optimization of experimental conditions to maximize signal-to-noise ratios, minimize sample degradation and enable single complex studies
2) The broader wavelength range available with the new laser source will expand the PI's ability to assess the importance of quantum coherence to the complete energy transfer pathway in purple bacteria
3) The broader wavelength range available with the new laser source will enable the PI to move beyond photosynthetic systems to examine quantum effects in mammalian metabolic processes in future work

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Final report: Acquisition of a Broadband Adjustable Repetition Rate Laser System for Investigations of Quantum Coherence in Biological Systems

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Upon receipt of the DURIP funding we ordered the adjustable repetition rate laser system (Spectra-physics Spirit laser with NOPA3H). This laser was delivered to the laboratory in March 2018 and it immediately replaced the previous 83 MHz titanium sapphire laser that we had been using.

1) The adjustable repetition rate of the proposed laser source will enable optimization of experimental conditions to maximize signal-to-noise ratios, minimize sample degradation and enable single complex studies

Upon installation of the laser we used it to create broadband light via continuum generation in a YAG crystal. This light was ideal for our investigations of quantum coherent phenomena in purple bacteria. With AFOSR funding we developed a highly sensitive form of two dimensional electronic spectroscopy that employs fluorescence detection (FD-2DES) and demonstrated the method on a coupled bacteriochlorophyll dimer that was designed as a simple system mimicking photosynthetic energy transfer[1]. We then proceeded to couple the FD-2DES experiment into a microscope to enable spatially resolved FD-2DES measurements. These are the first measurements of this type, and reveal detailed information about the electronic structure, quantum coherent processes and energy transfer pathways in purple bacteria *in vivo*. This work has recently been accepted to Nature Communications[2]. Representative data is shown in Figure 1. The strong cross-peak structure in the FD-2DES spectrum from purple bacteria displayed features that are distinctly different from those obtained in isolated light-harvesting complexes from purple bacteria using conventional 2DES. This caused considerable debate among the reviewers of our paper about the validity of our results. The new laser played a critical role by allowing us to perform repetition-rate-dependent experiments to rule out the possibility of long-lived states contributing to the unexpected cross-peak features.

With the new laser source we have been performing repetition-rate-dependent studies and have found that operation at 1MHz works well for reducing sample

photobleaching and the buildup of long-lived triplet states in purple bacteria. We have demonstrated the ability to collect high quality FD-2DES data from ~1000 molecules. In the upcoming months we plan to continue this work by varying the laser repetition rate and evaluating the effect on sensitivity. We expect to find an optimum repetition rate that maximizes sensitivity while maintaining high signal-to-noise ratios.

To reach the single molecule level we will employ a reduced dimensionality experiment employing a pulse-shaper to tailor the excitation of specific quantum coherences. We are currently waiting for the delivery of the pulse-shaper.

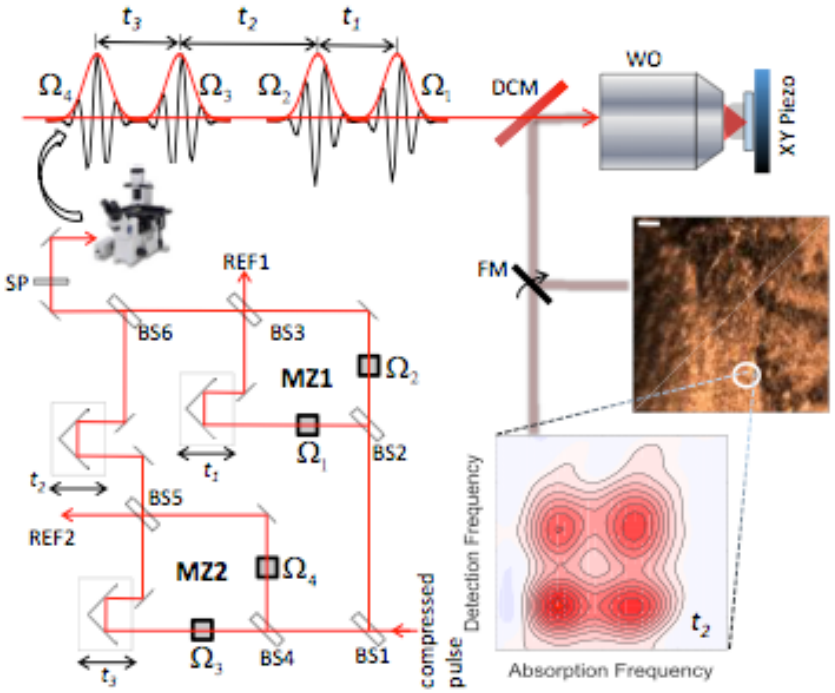

Figure 1: Spatially-resolved fluorescence-detected 2DES spectrometer[2]. A given pulse in the compressed laser pulse train is split 50:50 by a beam-splitter (BS1), and each half is routed into a Mach-Zehnder (MZ) interferometer (MZ1 and MZ2). Each of the four interferometer arms (two per MZ) contains an AOM which sweeps the carrier-envelope phase of the pulse. The time intervals between the four pulses are controlled by mechanical delay stages. One output port from each MZ is used to generate a reference signal which is utilized by the lock-in amplifier for signal detection. The other output port from each MZ is combined at BS6, generating four collinear time separated pulses (pump and probe pulse pairs), which are optically filtered by a shortpass filter (SP), and routed into a confocal microscope. A dichroic mirror (DCM) in the microscope transmits the collinear pulse train towards a water objective (WO), which focuses it on an immobilized sample. The sample is mounted on an XY scanning piezo stage (PZ). The fluorescence collected by the WO is separated from the excitation light at the DCM, and can be either routed for fluorescence imaging, or for generating a 2D map. An example of the fluorescence image, and the 2D spectrum at a desired XY location is shown in the figure. The 2D spectrum corresponds to zero waiting time between pump and probe pulse pairs and shows absorptive changes in the refractive index of the sample in the form of distinct 2D peakshapes. Cross peaks indicate that the absorption and detection frequencies of the system are different. This implies that the transitions corresponding to the positions of the two diagonal peaks correspond to excitonic transitions between sites which are electronically coupled on the excited state, and therefore connected via a common ground electronic state, and a common doubly-excited electronic state manifold.

2) The broader wavelength range available with the new laser source will expand the PI's ability to assess the importance of quantum coherence to the complete energy transfer pathway in purple bacteria

The new laser source allows us to expand our spectral range beyond our previous studies that focused on the light-harvesting 2 (LH2) complex in the 800-850 nm range[3]. The broader bandwidth allows us to easily reach 900 nm, enabling us to also examine the light-harvesting 1 (LH1) and the bacterial reaction center (BRC). Our FD-2DES data with the new laser source will provide insight into the electronic coupling throughout the entire photosynthetic network and will allow us to follow quantum coherent processes within and between the components of the system.

We employed the new laser to probe quantum coherence in LH2 in live bacteria. Representative data is shown in Figure 2, revealing a ~750 cm^{-1} coherent mode that dephases rapidly[4]. This particular frequency is resonant with the electronic energy gap between the B800 and B850 transitions in LH2. We are currently modeling this process and its assessing its role in energy transfer from B800 to B850.

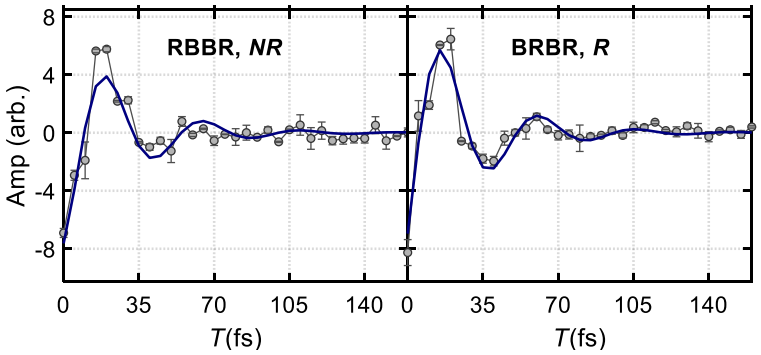

Figure 2: (Left) Nonrephasing (NR) and (Right) Rephasing (R) coherence signals obtained in purple bacteria. Fits to the data reveal a ~750 cm^{-1} coherence with a dephasing time of ~30 fs.

3) The broader wavelength range available with the new laser source will enable the PI to move beyond photosynthetic systems to examine quantum effects in mammalian metabolic processes in future work

With the new laser we can access the Q-band region of heme proteins as well as perform FD-2DES studies of bacteriorhodopsin as a model system for understanding the primary vision process in human rhodopsin. Figure 3 shows the broadband spectrum available with the new source, which will provide access to one and two photon transitions of interest in heme and rhodopsin systems. We are currently completing the pulse compression prior to our first FD-2DES measurements in this new spectral regime.

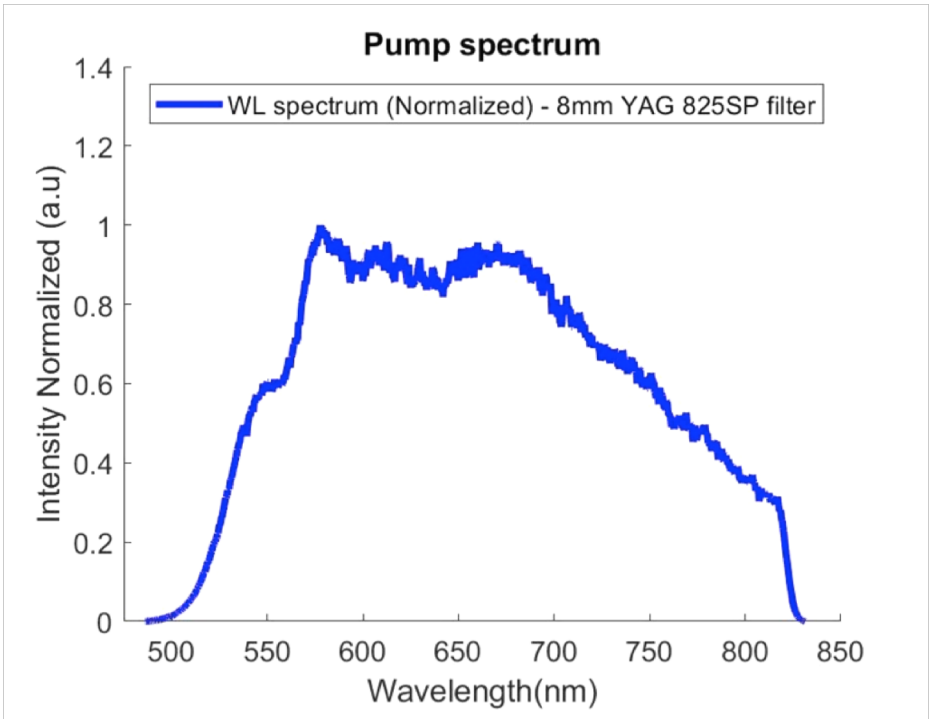

Figure 3: White light (WL) continuum spectrum generated in an 8mm YAG window, spanning relevant one and two photon transitions in heme proteins and in bacteriorhodopsin.

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