



Spectroscopic Studies of Photosynthetic Systems and Their Application in Photovoltaic Devices – Equipment Only

**Cooperative Research and Development
Final Report**

CRADA Number: CRD-06-175

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Cooperative Research and Development Final Report

In accordance with Requirements set forth in Article XI.A(3) of the CRADA document, this document is the final CRADA report, including a list of Subject Inventions, to be forwarded to the Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

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CRADA Title: Spectroscopic Studies of Photosynthetic Systems and Their Application in Photovoltaic Devices - Equipment Only

Parties to the Agreement: Kansas State University

Joint Work Statement Funding Table Showing DOE Commitment:

Estimated Costs	NREL Shared Resources
Year 1	\$ 20,000.00
Year 2	\$ 20,000.00
Year 3	\$ 20,000.00
TOTALS	\$ 60,000.00

Abstract of CRADA Work:

Spectral hole-burning (SHB) and single photosynthetic complex spectroscopy (SPCS) will be used to study the excitonic structure and excitation energy transfer (EET) processes of several photosynthetic protein complexes at low temperatures. The combination of SHB on bulk samples and SPCS is a powerful frequency domain approach for obtaining data that will address a number of issues that are key to understanding excitonic structure and energy transfer dynamics. The long-term goal is to reach a better understanding of the ultrafast solar energy driven primary events of photosynthesis as they occur in higher plants, cyanobacteria, purple bacteria, and green algae. A better understanding of the EET and charge separation (CS) processes taking place in photosynthetic complexes is of great interest, since photosynthetic complexes might offer attractive architectures for a future generation of circuitry in which proteins are crystallized.

Summary of Research Results:

Our key objective was to measure and interpret various photochemical and nonphotochemical hole-burned spectra and HB mechanism(s) in excitonically coupled natural photosynthetic complexes obtained in Dr. Seibert's group. (All samples were prepared by Dr. R. Picorel in Dr. M. Seibert's laboratory at NREL). The Jankowiak's group provided new insight into electronic structure and dynamics of all complexes of interest (see publication list). Over the years, due to loaned equipment and large amount of data generated, we were also able to further advance the description of HB and Δ FLN spectra where uncorrelated excitation energy transfer (EET) is present, a situation often encountered in photosynthetic complexes (e.g. CP43, PSI-CP43', CP47, etc.).

In addition, our collaborative research shed more light into electronic structure, photoconversion, frequency dependence of the Huang-Rhys (HR factor, S), spectral density, homogeneous/ inhomogeneous

broadening, EET, electron transfer (ET), and hole-burning (HB) mechanism(s) in several photosynthetic complexes. We also demonstrated that using Redfield theory adopted to HB spectroscopy provides a more rigorous description of excitonic structure and EET/ET processes in complex biological systems. The equipment borrowed from NREL (now abandoned at Kansas State University due to its age, i.e. most of the equipment has been retired and/or needs an expensive repair) also supported and in part continue to support the ongoing DOE funded research efforts in Prof. Jankowiak's laboratory at Kansas State University. In collaboration with Dr. M. Seibert, the following papers were published using borrowed equipment from NREL:

- N.C. Dang, V. Zazubovich, M. Reppert, B. Neupane, R. Picorel, M. Seibert, and R. Jankowiak, "The CP43 proximal Antenna Complex of Higher Plant Photosystem II Revisited: Modeling and Hole Burning Study (I)", *J. Phys. Chem. B.*, 112, 9921-33 (2008).
- B. Neupane, N. C. Dang, K. Acharya, M. Reppert, V. Zazubovich, R. Picorel, M. Seibert, and R. Jankowiak, "Insight into the Electronic Structure of the CP47 Antenna Protein Complex of the Photosystem II: Hole Burning and Fluorescence Study", *J. Am. Chem. Soc.*, 132, 4214-29 (2010).
- X. Feng, B. Neupane, K. Acharya, R. Picorel, M. Seibert, V. Zazubovich, and R. Jankowiak, "Spectroscopic Study of CP43' Complex and PSI-CP43' Supercomplex of the Cyanobacterium *Synechocystis PCC 6803*", *J. Phys. Chem. B* (2011) 115 (45):13339-49.
- N. Herascu, S. Ahmouda, R. Picorel, M. Seibert, R. Jankowiak and V. Zazubovich, "Effects of the Distributions of Energy Transfer Rates on Spectral Hole Burning in Pigment-Protein Complexes at Low Temperatures", *J. Phys. Chem. B* (2011) 115, 15098-15109.
- K. Acharya, B. Neupane, V. Zazubovich, R.T. Sayre, R. Picorel, M. Seibert, and R. Jankowiak, "Site-Energies of Active and Inactive Pheophytins in the Reaction Center of Photosystem II from *Chlamydomonas reinhardtii*" *J. Phys. Chem. B* (2012) 116, 3890-3899.
- M. Najafi, N. Herascu, M. Seibert, R. Picorel, R. Jankowiak, and V. Zazubovich, "Spectral Hole Burning, Recovery, and Thermocycling in Chlorophyll-Protein Complexes: Distributions of Barriers on the Protein Energy Landscape in CP43" *J. Phys. Chem B* (2012); DOI:10.1021/jp308055r.

In addition, during the CRADA signed between Dr. Seibert (NREL) and Prof. R. Jankowiak (KSU), about 50 additional papers were published by Dr. R. Jankowiak's group that, at least in part, took advantage from the equipment obtained from NREL. This work was supported by Jankowiak's individual DOE grants from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy (recent grant: DE-FG02-11ER16281; 2011-2014); the latter grant was recently extended for more two years (Sept. 1, 2014-Aug. 31, 2016).

Subject Inventions Listing:

N/A

This was a basic research in the area of photosynthesis.

Report Date:

September 14, 2014

Responsible Technical Contact at Alliance/NREL:

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