



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

**Cooperative Research and Development  
Final Report**

**CRADA Number: CRD-06-175**

NREL Technical Contact: Michael Seibert

**NREL is a national laboratory of the U.S. Department of Energy  
Office of Energy Efficiency & Renewable Energy  
Operated by the Alliance for Sustainable Energy, LLC**

This report is available at no cost from the National Renewable Energy  
Laboratory (NREL) at [www.nrel.gov/publications](http://www.nrel.gov/publications).

**CRADA Report**  
NREL/TP-2700-62883  
September 2014

Contract No. DE-AC36-08GO28308

## NOTICE

The submitted manuscript has been offered by an employee of the Alliance for Sustainable Energy, LLC (Alliance), a contractor of the US Government under Contract No. DE-AC36-08GO28308. Accordingly, the US Government and Alliance retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at [www.nrel.gov/publications](http://www.nrel.gov/publications).

Available electronically at <http://www.osti.gov/scitech>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
phone: 865.576.8401  
fax: 865.576.5728  
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
phone: 800.553.6847  
fax: 703.605.6900  
email: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
online ordering: <http://www.ntis.gov/help/ordermethods.aspx>

*Cover Photos: (left to right) photo by Pat Corkery, NREL 16416, photo from SunEdison, NREL 17423, photo by Pat Corkery, NREL 16560, photo by Dennis Schroeder, NREL 17613, photo by Dean Armstrong, NREL 17436, photo by Pat Corkery, NREL 17721.*

## **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.

**CRADA Number:** CRD-06-175

**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  $\Delta$ 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:**

Dr. Michael Seibert

**This document contains NO confidential, protectable, or proprietary information.**