Final Report (DE-FG02-08ER46504)

1. DOE award number, name, and address of the recipient (Institution):

DE-FG02-08ER46504; Paul R. Lowe, Assistant Vice President for Research, Kansas State University, Manhattan, KS 66505.

2. Project Title and name of the Principal Investigator:

Title: Excitation energy transfer in natural photosynthetic complexes and chlorophyll trefoils: hole-burning and single complex/trefoil spectroscopic studies.

Principal Investigator: Ryszard Jankowiak, Kansas State University, Department of Chemistry, CBC Bldg., Manhattan KS, 66505; Phone: (785) 532-6785; E-mail: ryszard@ksu.edu

3. Date of the report and award period covered by the report with approved budget amount:

07/01/2009-06/30/2012 (with six months no cost extension granted by DOE)

4. A brief description (abstract) of project goal and objective.

In this project we studied both natural photosynthetic antenna complexes and various artificial systems (e.g. chlorophyll (Chl) trefoils) using high resolution hole-burning (HB) spectroscopy and excitonic calculations. Results obtained provided more insight into the electronic (excitonic) structure, inhomogeneity, electron-phonon coupling strength, vibrational frequencies, and excitation energy (or electron) transfer (EET) processes in several antennas and reaction centers. For example, our recent work provided important constraints and parameters for more advanced excitonic calculations of CP43, CP47, and PSII core complexes. Improved theoretical description of HB spectra for various model systems offers new insight into the excitonic structure and composition of low-energy absorption traps in very several antenna protein complexes and reaction centers. We anticipate that better understanding of HB spectra obtained for various photosynthetic complexes and their simultaneous fits with other optical spectra (i.e. absorption, emission, and circular dichroism spectra) provides more insight into the underlying electronic structures of these important biological systems. Our recent progress provides a necessary framework for probing the electronic structure of these systems via Hole Burning Spectroscopy. For example, we have shown that the theoretical description of non-resonant holes is more restrictive (in terms of possible site energies) than those of absorption and emission spectra. We have demonstrated that simultaneous description of linear optical spectra along with HB spectra provides more realistic site energies. We have also developed new algorithms to describe both nonresonant and resonant hole-burn spectra using more advanced Redfield theory. Simultaneous description of various optical spectra for complex biological system, e.g. artificial antenna systems, FMO protein complexes, water soluble protein complexes, and various mutants of reaction centers continues; this work is supported by the new DOE BES grant.

5. A description of accomplishments over the three-year period and their significance to the field

Progress since the last progress report:

- During the last year of this project we focused on theoretical description of various optical spectra using the Redfield theory. The simulated hole-burned spectra within this approach account for the influences of electron-phonon (el-ph) coupling and lifetime broadening, which includes explicitly the effects of excitonic interactions and energy transfer on hole-shapes and provide more insight into the dynamics of these complex biological systems. The primary challenge is to simultaneously fit

various above spectra to obtain the correct set of pigment site energies (i.e. transition frequencies in the absence of inter-pigment coupling) that are critical to properly describe excitonic structure (manuscript in preparation).

▪ Preliminary modeling of various optical spectra (absorption, fluorescence, hole-burned and CD spectra) for CP43 and CP47 have been completed The simulated hole-burned spectra within this approach account for the influences of electron-phonon (el-ph) coupling and lifetime broadening, which includes explicitly the effects of excitonic interactions and energy transfer on hole shapes (manuscripts in preparation). The primary challenge is to simultaneously fit various above spectra to obtain the correct set of pigment site energies (i.e. transition frequencies in the absence of inter-pigment coupling) that are critical to properly describe excitonic structure.

▪ A model has been developed to describe resonant fluorescence line-narrowed (FLN) and hole-burned (HB) spectra in the presence of excitation energy transfer. Calculations are in good agreement with experimental data (not shown) obtained in the literature for various photosynthetic complexes (manuscript in preparation). An example of FLN and HB spectra for a simple dimer is shown below. Calculations can be expanded for complexes with many pigments.

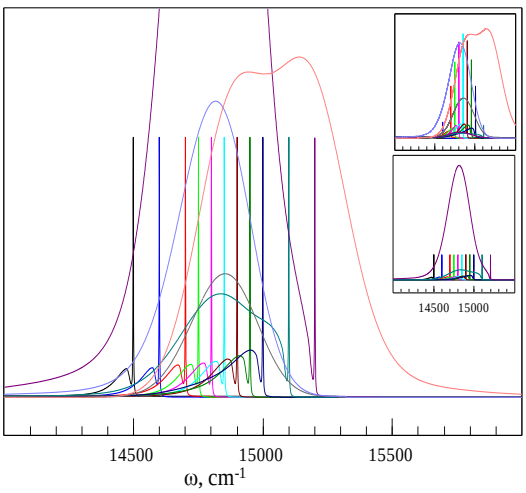

Figure 1. Calculated FLN spectra for weakly coupled dimers for a model dimer. in the presence of excitation energy transfer to the trap. The main frame shows trap state (——, $L_A(\omega) + L_B(\omega)$), bulk absorption (——) and bulk emission (——). Rest are FLN spectra normalized at the intensity of ZPLs. Excitation frequencies for these spectra are (with ZPLs from left to right) 14500, 14600, 14700, 14750, 14800, 14850, 14900, 14950, 15000, 15100, and 15200 cm^{-1}, respectively. Upper frame of inset shows the relative intensities of ZPLs with comparison of trap state (——), bulk absorption (——) and bulk emission (——). Lower frame of inset shows the full graph of FLN spectra in the main frame.

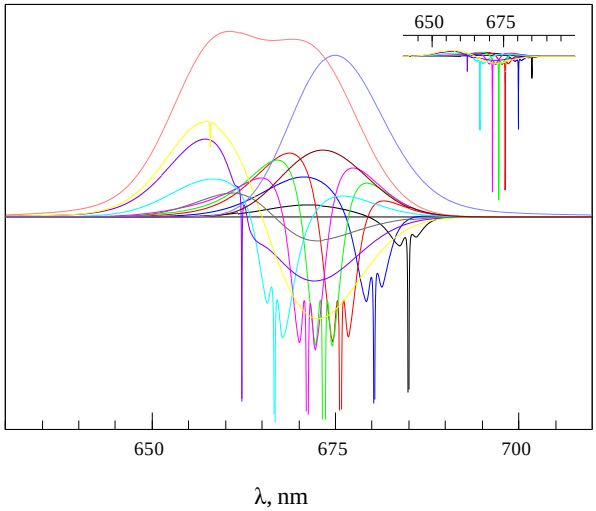

Figure 2. Calculated resonant hole-burned (HB) spectra for weakly coupled dimers with the excitation energy transfer . The main frame shows trap state (——, $L_A(\omega) + L_B(\omega)$), NRHB (——), bulk absorption (——) and bulk emission (——). Rest are RHB spectra. ZPHs are cut-off to better resolve PSBHs. λ_{burn} for these spectra are (with ZPHs from right to left) 684.93 nm (——), 680.27 nm (——), 675.68 nm (——), 673.40 nm (——), 671.14 nm (——), 666.68 nm (——), 662.25 nm (——), and 657.89 nm (——). Inset shows the relative intensities of ZPHs.

This model will allow to analyze various shapes of hole-burned spectra in complex photosynthetic systems and extract proper electron-phonon coupling parameters for future excitonic calculations.

▪ ***Single-site parameters.*** A challenge in spectroscopic applications to photosynthetic complexes is to obtain detailed information on the "single-site" spectral profile, i.e. the absorption or emission spectrum of individual molecules. In measured bulk spectra, the single-site spectrum (SSS) is obscured by convolution with a distribution function, which results from differences in the micro environments of individual molecules in a sample. We have developed numerical Fourier transform deconvolution methods to obtain the SSS from bulk absorption and emission spectra and the distribution function. We continue to test this approach on experimental data (research in progress).

The method relies on matching the low-frequency region of the distribution function to the absorption spectrum. It is anticipated that the Franck-Condon factor α (a crucial parameter in the SSS) can be approximated by the ratio of the total area under the scaled distribution function to the area under the absorption spectrum.

▪ ***Non-resonant HB spectra.*** Theoretical description of fluence dependent non-resonant HB spectra obtained for various excitonically coupled systems has been completed (manuscript in preparation). We anticipate that better understanding of HB spectra obtained for various photosynthetic complexes and their simultaneous fits with other optical spectra will provide more insight into the underlying electronic structure and dynamics of these complex biological systems.

A description of accomplishments of the entire project (summary)

▪ We have developed programs and algorithms to fit resonant and nonresonant hole-burned (HB) spectra obtained for various photosynthetic complexes. In addition, theories (models) have been developed to describe theoretically HB spectra in the presence of excitation energy transfer (EET); to be published (manuscript in preparation). All these developments are currently applied in our research to advance understanding of excitonic structure of complex biological photosynthetic proteins; the current work is supported by our new DOE Grant Number: DE-FG02-11ER16281.

▪ Using HB spectroscopy, we showed that EET time in ethynyl-linked chlorophyll trefoil (ChlT1) monomer is very fast (~2.5 ps) at liquid helium temperature. This is consistent with data obtained by femtosecond transient spectroscopy experiments performed at room temperature, in which an EET time of 1.8 ps was observed. This finding further supports the importance of through-bond electronic coupling at low temperature. In addition, we showed that ChlT1 (even at very low concentrations) in methyl trahydrofuranethanol glass (1:200 v/v; T ~ 5 K) forms different types of aggregates. It was demonstrated that the relative distribution of various types of aggregates depends on the cooling rate and matrix composition. For example, the EET time in two types of ChlT1-based aggregates was slower by a factor of ~57 with respect to that observed for ChlT1 monomer. This indicates that ChlT1 aggregates can retain ultrafast energy transfer properties similar to those observed in natural photosynthetic antennas. It is anticipated that such building blocks could be utilized in future photovoltaic devices. *J. Phys. Chem. B* **2011**, *115*, 10391-10399.

▪ We also demonstrated that the band near 684 nm (in CP47) previously observed in singlet-minus-triplet spectra originates from a subpopulation of partially destabilized complexes with lowest-energy traps located near 684 nm in absorption (referred to as AT2) giving rise to FT2 emission. It was demonstrated that varying contributions from the F1, FT1, and FT2 emission bands led to different maxima of fluorescence spectra reported in the literature. The fluorescence spectra were consistent with the zero-phonon hole action spectra obtained in absorption mode, the profiles of the non-resonantly burned holes as a function of fluence, as well as the fluorescence line-narrowed spectra obtained for the Q_y band. The lowest Q_y state in absorption band (A1) was characterized by an electron-phonon coupling with the Huang-Rhys factor S of ~1 and an inhomogeneous width of ~180 cm^{-1}. The mean phonon frequency of the A1 band is 20 cm^{-1}. In contrast to previous observations, intact isolated CP47 revealed negligible contribution from the triplet- bottleneck hole, i.e., the AT2 trap. It has been shown that Chls in intact CP47 are connected via efficient excitation energy transfer to the A1 trap near 693 nm and that the position of the fluorescence maximum depends on the burn fluence. That is, the 695 nm fluorescence maximum shifts blue with increasing fluence, in agreement with nonresonant hole burned spectra. The above findings provide important constraints and

parameters for excitonic calculations, which in turn should offer new insight into the excitonic structure and composition of low-energy absorption traps. *J. Am. Chem. Soc.* **2010** *132*, 4214–4229.

▪ We also presented simulated steady-state absorption, emission, and nonresonant hole burning (HB) spectra for the CP47 antenna complex of photosystem II (PS II) based on fits to recently refined experimental data (Neupane et al. *J. Am. Chem. Soc.* **2010**, *132*, 4214). Excitonic simulations were based on the 2.9 Å resolution structure of the PS II core from cyanobacteria (Guskov et al. *Nat. Struct. Mol. Biol.* **2009**, *16*, 334), and allowed for preliminary assignment of the chlorophylls (Chls) contributing to the lowest excitonic states. The search for realistic site energies was guided by experimental constraints and aided by simple fitting algorithms. The following experimental constraints were used: (i) the oscillator strength of the lowest-energy state should be approximately ≤ 0.5 Chl equivalents; (ii) the excitonic structure must explain the experimentally observed red-shifted (~695 nm) emission maximum; and (iii) the excitonic interactions of all states must properly describe the broad (non-line-narrowed, NLN) HB spectrum (including its antihole) whose shape is extremely sensitive to the excitonic structure of the complex, especially the lowest excitonic states. Importantly, our assignments differed significantly from those previously reported by Raszewski and Renger (*J. Am. Chem. Soc*. **2008**, *130*, 4431), due primarily to differences in the experimental data simulated. In particular, we found that the lowest state localized on Chl 526 possesses too high of an oscillator strength to fit low-temperature experimental data. Instead, we suggested that Chl 523 most strongly contributes to the lowest excitonic state, with Chl 526 contributing to the second excitonic state. Since the fits of nonresonant holes are more restrictive (in terms of possible site energies) than those of absorption and emission spectra, we suggest that fits of linear optical spectra along with HB spectra provide more realistic site energies. *J. Phys. Chem. B* **2010**, *114*, 11884–11898.

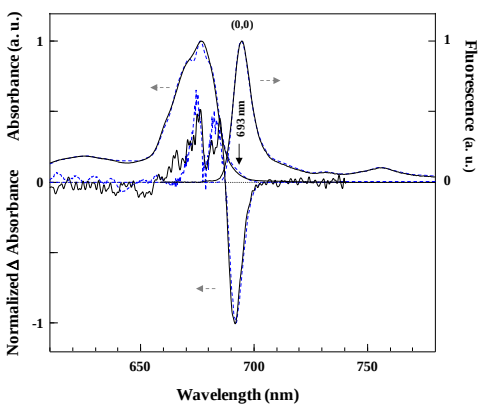

Figure 3. Best fits (blue dashed curves) to the experimental absorption, emission, and NLN hole burned spectra (black curves). In the fit shown, the lowest state resides mainly on Chl 523 while Chl 526 contributes strongly to the second lowest state.

▪ We have also demonstrated that the fluorescence origin band maximum (~695nm) of the intact CP47 antenna protein complex of PSII from spinach does not shift in the temperature range of 5-77 K. Theoretical description was in perfect agreement with experimental data. However, emission shifts continuously to shorter wavelengths (~692 nm) if high fluence is used, and hole burning takes place. This was shown to be in agreement with hole-burning theories. If permanent damage does not occur, this process is reversible by cycling the temperature. We showed that the emission peaks previously observed near 685 and 691 nm are characteristic of destabilized complexes and cannot be eliminated by temperature cycling. We argued that the CP47 complex is extremely light sensitive at low temperatures and that its 695 nm emission band in the PSII core, in contrast to several literature reports, does not arise from excitations that are trapped on red-absorbing chlorophyll of the ~690 nm band, as 5 K emission of intact (non-aggregated) CP47 also peaks near 695 nm. *J. Phys. Chem. Lett.* **2010**, *1*, 2310-2315.

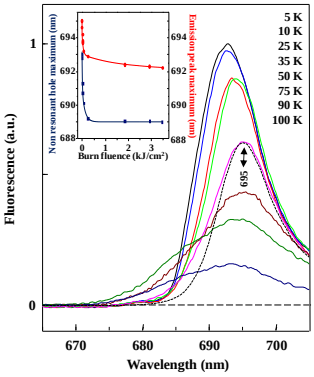

Figure 4. Temperature dependence of the fluorescence spectrum (top curve) obtained for sample with saturated non-resonant hole at 5 K; its maximum is near 692 nm. The remaining spectra were obtained at higher

temperatures, i.e. 10, 25, 35, 50, 75, 90, and 100 K. The dotted curve is the pre-burn 50 K spectrum from Figure 2 frame B scaled for comparison with the post-burn curve. The inset show the shifts of the broad non-resonant holes (blue squares) and positions of the corresponding maxima of the origin bands (red circles), obtained at different burn fluences.

- In light of very recent developments all spectra obtained for CP43 and CP47 are being recalculated using more advanced Redfield theory. The simulated hole-burned spectra within this approach account for the influences of electron-phonon (el-ph) coupling and lifetime broadening, which includes explicitly the effects of excitonic interactions and energy transfer on hole shapes (manuscripts in preparation). The primary challenge is to simultaneously fit various above spectra to obtain the correct set of pigment site energies (i.e. transition frequencies in the absence of inter-pigment coupling) that are critical to properly describe excitonic structure.

- Accurate lineshape functions for modeling fluorescence line narrowing (FLN) difference spectra (ΔFLN spectra) in the low-fluence limit were derived and examined in terms of the physical interpretation of various contributions, including photoproduct absorption and emission. While in agreement with the earlier results of Jaaniso [Proc. Est. Acad. Sci., Phys., Math. **34**, 277 (1985)] and Fünfschilling *et al.* [J. Lumin. **36**, 85 (1986)], the derived formulas differ substantially from functions used recently [e.g., M. Rätsep *et al.*, Chem. Phys. Lett. **479**, 140 (2009)] to model ΔFLN spectra. In contrast to traditional FLN spectra, we have demonstrated that for most physically reasonable parameters, the ΔFLN spectrum reduces simply to the single-site fluorescence lineshape function. These results imply that direct measurement of a bulk-averaged single-site fluorescence lineshape function can be accomplished with no complicated extraction process or knowledge of any additional parameters such as site distribution function shape and width. We argued that previous analysis of ΔFLN spectra obtained for many photosynthetic complexes led to strong artificial lowering of apparent electron-phonon coupling strength, especially on the high-energy side of the pigment site distribution function. *J. Chem. Phys.* **2010**, *133*, 014506/1 – 014506/9.

- We also developed exact equations for the low-fluence non-line-narrowed (NLN) nonphotochemical hole-burning (NPHB) spectrum of an excitonically coupled dimer (for arbitrary coupling strength) under the assumption that postburn and preburn site energies are independent. The equations provide a transparent view into the contributions of various effects to the NPHB spectrum. We have demonstrated that the NPHB spectrum in dimers is largely dominated by the statistical reshuffling of site energies and by altered excitonic transition energies of *both* excitonic states (in contrast with only the lowest state). For comparison of these results with those from larger excitonically coupled systems, the low-fluence NLN NPHB spectrum obtained for the CP47 complex (a 16-pigment core antenna complex of Photosystem II) is also calculated using Monte Carlo simulations. In this larger system it was shown that the NPHB spectra for individual excitonic states are not entirely conservative (although the changes in average oscillator strength for the higher excitonic states are in most cases less than 1%), a feature which we argued is due primarily to reordering of the contributions of various pigments to the excitonic states. We anticipate that a better understanding of NPHB spectra obtained for various photosynthetic complexes and their simultaneous fits with other optical spectra (e.g., absorption, emission, and circular dichroism spectra) will provide more insight into the underlying electronic structures of various photosynthetic systems. *J. Chem. Phys.* **2009,** *131*, 234104/1 – 234104/8.

- The CP43 core antenna complex of PSII is known to possess two quasi-degenerate “red”-trap states. It has been suggested recently (Zazubovich, V.; Jankowiak, R. *J. Lumin.* **2007**, *127*, 245) that the site distribution functions of the red states (A and B) are uncorrelated and that narrow holes are

burned in the subpopulations of chlorophylls (Chls) from states A and B that are the lowest-energy Chl in their complex and previously thought not to transfer energy. This model of uncorrelated excitation energy transfer (EET) between the quasidegenerate bands was expanded by taking into account both electron-phonon and vibrational coupling. The model is applied to fit simultaneously absorption, emission, zero-phonon action, and transient hole burned (HB) spectra obtained for the CP43 complex with minimized contribution from aggregation. It was demonstrated that the above listed spectra can be well fitted using the uncorrelated EET model, providing strong evidence for the existence of efficient energy transfer between the two lowest energy states, A and B (either from A to B or from B to A), in CP43. Possible candidate Chls for the low-energy A and B states were discussed, providing a link between CP43 structure and spectroscopy. Finally, we proposed that persistent holes originate from regular NPHB accompanied by the redistribution of oscillator strength due to excitonic interactions, rather than photoconversion involving Chl-protein hydrogen bonding, as suggested before (Hughes J. L. et al. *Biochemistry* **2006**, *45*, 12345). In the accompanying paper (Reppert, M.; Zazubovich, V.; Dang, N. C.; Seibert, M.; Jankowiak, R. *J. Phys.Chem. B* **2008**, 9934), we have demonstrated that our model is consistent with excitonic calculations, which also provide very good fits to both transient and persistent HB spectra obtained under non-line-narrowing conditions. J. Phys. Chem. **2008,** *112*, 9921-9933.

- The CP43 protein complex of the core antenna of higher plant photosystem II (PSII) has two quasidegenerate "red" absorption states. We have shown (see: Dang, N. C., et al. *J. Phys. Chem. B* **2008**, *112*, 9921) that the site distribution functions (SDFs) of red-states A and B are uncorrelated and the narrow holes are burned in *subpopulations* of chlorophylls (Chls) from states A and B that are the lowest energy pigments in their particular CP43 complexes and cannot further transfer energy downhill. We have also shown the results of a series of Monte Carlo simulations using the 3.0-Å structure of the PSII core complex from cyanobacteria (Loll, B., et al. *Nature* **2005**, *303*, 1040.) where we modeled absorption, emission, persistent, and transient hole burned (HB) spectra. At the current structural resolution, we found calculated site energies (obtained from INDO/S calculations) to be only suggestive because their values are different for the two monomers of CP43 in the PS II dimer. As a result, to probe the excitonic structure, a fitting algorithms were developed to optimize Chl site energies from various starting values corresponding to different A/B pigment combinations to provide simultaneously good fits to several types of optical spectra. We demonstrated that the shape of the calculated absorption, emission, and transient/persistent hole-burned spectra is consistent with experimental data and our model for excitation energy transfer between two quasi-degenerate lowest-E states (A and B) with uncorrelated SDFs discussed in other papers supported by this project. Calculations revealed that absorption changes observed near 670 nm in the non-line-narrowed persistent HB spectra (assigned to photoconversion involving Chl-protein hydrogen-bonding by Hughes (*Biochemistry* **2006**, *45*, 12345.) are most likely the result of nonphotochemical hole-burning (NPHB) accompanied by the redistribution of oscillator strength due to modified excitonic interactions. We argued that a unique redistribution of oscillator strength during the NPHB process helps to assign Chls contributing to the low-energy states. It was demonstrated that the 4.2 K asymmetric triplet-bottleneck (transient) hole was mostly contributed to by both A and B states, with the hole profile described by a sub-ensemble of pigments, which were the lowest-energy pigments (Bs- and As-type) in their complexes. On the basis of our excitonic calculations, the best Chl candidates that contributed to the low-energy A and B states were Chl 44 and Chl 37, respectively (J. Phys. Chem. B **2008,** *112*, 9934-9947.) More advanced excitonic theories are being currently used to describe various optical spectra of several protein complexes.

- **LHCII calculations.** Our approach for identifying low-energy states in the various antenna complexes and reaction centers has two major components. The first involves simple Monte Carlo

modeling of experimental data using coupling constants obtained from the known crystal structures of the complex. Coupling constants are calculated using various approaches and the model is first tested with better known LHCII complex. The second approach involves more advance excitonic calculations, i.e. using the Redfield theory adapted to describe HB spectra. Our calculations have identified two Chl a/Chl b pairs which could potentially produce resonant and nonresonant holes, but the configurational space has not been exhausted. More advanced spectral simulations are currently underway to identify which of these strongly coupled pairs may contribute to the lowest-energy state. This methodology is currently applied to CP29, which is simpler, as it does not exist as a trimer.

- **Non-resonant HB spectra.** We continue to work on theoretical description of fluence dependent non-resonant HB spectra obtained for various excitonically coupled systems. We anticipate that better understanding of HB spectra obtained for various photosynthetic complexes and their simultaneous fits with other optical spectra will provide more insight into the underlying electronic structure and dynamics of these complex biological systems.

6. A list of papers in which DOE support (DE-FG02-08ER46504) is acknowledged:

1) B. Neupane, N. C. Dang, R. F. Kelley, M. R. Wasielewski, and R. Jankowiak, "Low Temperature Frequency Domain Study of Excitation Energy Transfer in Ethynyl-linked Chlorophyll-trefoils and Aggregates", *J. Phys. Chem. B* **2011**, *115*, 10391-10399.
2) B. Neupane, N. Dang, M. Reppert, K. Acharya, V. Zazubovich, R. Picorel, M. Seibert, and R. Jankowiak, "Insight into the Electronic Structure of the CP47 Antenna Protein Complex of Photosystem II: Hole Burning and Fluorescence Study", *J. Am. Chem. Soc.* **2010** *132*, 4214–4229.
3) M. Reppert, K. Acharya, B. Neupane, and R. Jankowiak, "Lowest electronic states of the CP47 antenna protein complex of PSII: simulation of optical spectra and revised structural assignments", *J. Phys. Chem. B* **2010**, *114*, 11884–11898.
4) K. Acharya, B. Neupane, M. Reppert, X. Feng, and R. Jankowiak, "On the Unusual Temperature Dependent Emission of the CP47 Antenna Protein Complex of Photosystem II", *J. Phys. Chem. Lett.* **2010**, *1*, 2310-2315.
5) M. Reppert, V. Naibo, and R. Jankowiak, Accurate Modeling of Fluorescence Line Narrowing Difference Spectra: Direct Measurement of the Single-Site Fluorescence Spectrum", *J. Chem. Phys.* **2010**, *133*, 014506/1 – 014506/9.
6) M. Reppert, V. Naibo, and R. Jankowiak, "Analytical formulas for low-fluence non-line-narrowed hole-burned spectra in an excitonically coupled dimer", *J. Chem. Phys.* **2009,** *131*, 234104/1 – 234104/8.
7) 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. **2008,** *112*, 9921-9933.
8) M. Reppert, N.C. Dang, V. Zazubovich, M. Seibert, and R. Jankowiak, Low-Energy Chlorophyll States in the CP43 Antenna Protein Complex: Simulation of Various Optical Spectra. II J. Phys. Chem. B **2008,** *112*, 9934-9947.

Research supported by the DOE EPSCoR (DE-FG02-08ER46504 grant) led to the recently published reviews (mostly supported by the new DOE BES grant DE-FG02-11ER16281).

9) R. Jankowiak, Invited Perspective for J. Phys. Chem. Lett. "*Charge separation pathways in Photosystem II"* (2012) **3**, 1684-1694.
10) R. Jankowiak, M. Reppert, V. Zazubovich, J. Pieper, and T. Reinot; Invited review: "Site Selective and Single Complex Laser-Based Spectroscopies: A Window on Excited State Electronic Structure, Excitation Energy Transfer, and Electron-Phonon Coupling of Selected Photosynthetic Complexes", Chem. Reviews (2011) 111, 4546-4598.

Data supported by the DE-FG02-08ER46504 grant were reported at several national and international conferences.

7. A total list of people who worked on the project:

The names and average percentage of support for those funded from DOE EPSCoR DE-FG02-08ER46504 (GOCH001082) are as follows:

Ryszard J. Jankowiak (Professor & PI) - partial support @ 11%
Khem Acharya (Graduate Student) - partial support @ 56%
Nhan C. Dang (Post-Doctoral Research Associate) - partial support @ 37%
Isaac S. Fees (Undergraduate Student) - partial support @ 11%
Ximao Feng (Post-Doctoral Research Associate) - partial support @ 62%
Mukund B. Koirala (Graduate Student) - partial support @ 32%
Bhanu B. Neupane (Graduate Student) - partial support @ 12%
Mike E. Reppert (Undergraduate Student) - partial support @ 59%

***Collaborators* (no cost to this project)**
Michael Seibert, National Renewable Energy Laboratory, NREL, Golden, CO.
Michael Wasielewski, Department of Chemistry, Northwestern University, Evanston, IL.
Virginia Naibo, Department of Mathematics, Kansas State University.

8. An updated list of other support (current and pending, federal and non-federal.) For each, indicate the overlap:

Source of Support: US Department of Energy (Basic Energy Sciences)
Total Award Amount: $480,000
Total Award Period Covered: 9/1/11-8/31/14
Project/Proposal Title: *Resonant and Non-resonant Hole-burning and Delta Fluorescence Line-narrowing Study of BCh1s in Excitonically Coupled Photosynthetic Systems*.
No overlap (although methodologies developed during the funding period of the DE-FG02-08ER46504 grant will be used in the current DOE BES project). Here research focuses on WSCP and FMO complexes.

Source of Support: National Science Foundation (NSF)
Total Award Amount: $380,000
Total Award Period Covered: 7/15/09-6/30/13
Project/Proposal Title: *Comparative Studies of Electronic Structure and Dynamic Process in Model Photosynthetic Complexes Using Spectral Hole Burning and Single Complex Spectroscopies*.

No overlap; this project focuses on spectral hole-burning and single photosynthetic complex spectroscopy to study excitonic structure and excitation energy transfer (EET) processes in PSI-C43′ supercomplexes and the PSII core from the cyanobacterium *Synechocystis*.

Source of Support: Kansas Technology Enterprise Corporation (KTEC)
Total Award Amount: $37,493
Total Award Period Covered: 6/30/08-09/30/12
Project/Proposal Title: *Excitation Energy Transfer in Natural Photosynthetic Complexes and Chlorophyll Trefoils: Hole Burning and Single Complex/Trefoil Spectroscopic Studies*
This was the matching funding for the DE-FG02-08ER46504 grant from KTEC.

Pending funding ($472,073**) submitted to NSF in 2012:**

Source of Support: National Science Foundation (NSF)
Total Award Amount: $472,073
Total Award Period Covered: 5/1/13-4/30/16
Project/Proposal Title: *Electronic Structure and Dynamic Process in Light Harvesting Proteins and Reaction Center of Photosystem II.*
No overlap; here the proposed research will focus on various mutants and/or modified antennas for future photovoltaic devices.

9. Cost status: Show approved budget for the full budget period and actual costs incurred. For cost-sharing, breakout by DOE share, recipient share and total costs. Financial Statements should be reported to DOE Chicago Operations as requested.

Attached below is the final SF425 that was sent to DOE on 08/01/2012. The final approved budget was $450,000.00 and this was also the final expenditure amount. The recipient share budget was $45,000.00 and K-State (Roger D. McBride, Assistant Director, Sponsored Programs, Division of Financial Services, Kansas State University 10 Anderson Hall, Manhattan, KS 66506-0108, 785-532-1848 (office), 785-532-3640(fax) reported expenditures of $46,334.77. Total costs of the project then show as $496,334.77.

799415

FEDERAL FINANCIAL REPORT

(Follow form instructions)

1. Federal Agency and Organizational Element to Which Report is Submitted	2. Federal Grant or Other Identifying Number Assigned by Federal Agency (To report multiple grants, use FFR Attachment)	Page	of
US DEPARTMENT OF ENERGY	DE-FG02-08ER46504	1	1 pages

3. Recipient Organization (Name and complete address including Zip code)
KANSAS STATE UNIVERSITY
DIVISION OF FINANCIAL SERVICES - SPONSORED PROGRAMS, ANDERSON HALL ROOM 10, MANHATTAN KS 66506-0108

4a. DUNS Number	4b. EIN	5. Recipient Account Number or Identifying Number (To report multiple grants, use FFR Attachment)	6. Report Type	7. Basis of Accounting
92 977-3554	48-0771751	EC9994	☐ Quarterly ☐ Semi-Annual ☐ Annual ☑ Final	☑ Cash ☐ Accrual

8. Project/Grant Period From: (Month, Day, Year)	To: (Month, Day, Year)	9. Reporting Period End Date (Month, Day, Year)
7/1/2008	6/30/2012	6/30/2012

10. **Transactions**	Cumulative
(Use lines a-c for single or multiple grant reporting)	
Federal Cash (To report multiple grants, also use FFR Attachment):	
a. Cash Receipts	449,689.00
b. Cash Disbursements	450,000.00
c. Cash on Hand (line a minus b)	-311.00
(Use lines d-o for single grant reporting)	
Federal Expenditures and Unobligated Balance:	
d. Total Federal funds authorized	450,000.00
e. Federal share of expenditures	450,000.00
f. Federal share of unliquidated obligations	0.00
g. Total Federal share (sum of lines e and f)	450,000.00
h. Unobligated balance of Federal funds (line d minus g)	0.00
Recipient Share:	
i. Total recipient share required	45,000.00
j. Recipient share of expenditures	46,334.77
k. Remaining recipient share to be provided (line i minus j)	-1,334.77
Program Income:	
l. Total Federal program income earned	0.00
m. Program income expended in accordance with the deduction alternative	0.00
n. Program income expended in accordance with the addition alternative	0.00
o. Unexpended program income (line l minus line m or line n)	0.00

	a. Type	b. Rate	c. Period From	Period To	d. Base	e. Amount Charged	f. Federal Share
11. Indirect Expense	Predetermined	46.00	7/1/2008	6/30/2012	300,360.82	138,169.63	138,169.63
		0.00			0.00	0.00	0.00
				g. Totals:	300,360.82	138,169.63	138,169.63

12. *Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation:*

13. Certification: By signing this report, I certify that it is true, complete, and accurate to the best of my knowledge. I am aware that any false, fictitious, or fraudulent information may subject me to criminal, civil, or administrative penalities. (U.S. Code, Title 18, Section 1001)

a. Typed or Printed Name and Title of Authorized Certifying Official	c. Telephone (Area code, number and extension)
Roger D. McBride, Asst. Director Sponored Programs	785-532-6207
	d. Email address roger57@k-state.edu
b. Signature of Authorized Certifying Official Roger D. McBride	e. Date Report Submitted (Month, Day, Year) 8/1/2012
	14. Agency use only:

Standard Form 425
OMB Approval Number: 0348-0061
Expiration Date: 10/31/2011

Paperwork Burden Statement
According to the Paperwork Reduction Act, as amended, no persons are required to respond to a collection of information unless it displays a valid OMB Control Number. The valid OMB control number for this information collection is 0348-0061. Public reporting burden for this collection of information is estimated to average 1.5 hours per response, including time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding the burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to the Office of Management and Budget, Paperwork Reduction Project (0348-0060), Washington, DC 20503.