

and in aggregates, which are widely used to mimic the quenching state *in vivo*. The experiments identify several quenching sites in the aggregates.

#### 888-Pos

##### Effect of Antenna-Depletion in Photosystem II on Excitation Energy Transfer in *Arabidopsis thaliana*

Herbert van Amerongen<sup>1</sup>, Bart van Oort<sup>1</sup>, Marieke Alberts<sup>1</sup>,

Silvia de Bianchi<sup>2</sup>, Luca Dall'Osto<sup>2</sup>, Roberto Bassi<sup>2</sup>,

Gediminas Trinkunas<sup>3</sup>, Roberta Croce<sup>4</sup>.

<sup>1</sup>Wageningen University, Wageningen, Netherlands, <sup>2</sup>University of Verona, Verona, Italy, <sup>3</sup>Institute of Physics, Vilnius, Lithuania, <sup>4</sup>University of Groningen, Groningen, Netherlands.

The role of individual photosynthetic antenna complexes of Photosystem II (PSII) both in membrane organization and excitation energy transfer have been investigated. Thylakoid membranes from wild-type (WT) *Arabidopsis thaliana*, and three mutants lacking light-harvesting complexes CP24, CP26 or CP29, respectively, were studied by picosecond-fluorescence spectroscopy. By using different excitation/detection wavelength combinations it was possible for the first time to separate PSI and PSII fluorescence kinetics. The sub-100 ps component, previously ascribed entirely to PSI, turns out to be partly due to PSII. Moreover, the migration time of excitations from antenna to PSII reaction center (RC) was determined for the first time for thylakoid membranes. It is four times longer than for PSII-only membranes, due to additional antenna complexes, which are less well connected to the RC. The results in the absence of CP26 are very similar to those of WT, demonstrating that the PSII organization is not disturbed. However, the kinetics in the absence of CP29 and, especially, of CP24 show that a large fraction of the light-harvesting complexes becomes badly connected to the RCs. Interestingly, the excited-state lifetimes of the "disconnected" light-harvesting complexes appear to be substantially quenched.

#### 889-Pos

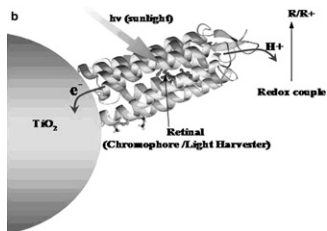
##### Spectroscopic Determination of HOMO and LUMO Energies of Retinal in Bacteriorhodopsin for Solar Cell Applications

Gau Xingyu<sup>1</sup>, Surya N. Viswanathan<sup>2</sup>, Chih-Wei Chang<sup>2,3</sup>,

Bernardo Barbiellini<sup>2</sup>, David E. Budil<sup>2</sup>, Venkatesan Renukopalakrishnan<sup>2,3</sup>.

<sup>1</sup>National University of Singapore, Singapore, Singapore, <sup>2</sup>Northeastern University, Boston, MA, USA, <sup>3</sup>Children's Hospital, Harvard Medical School, Boston, MA, USA.

Bacteriorhodopsin (bR) is a potential sensitizer for bio-sensitized solar cells (Fig. 1). In this study, the energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of retinal in bR are investigated using X-ray Photoemission Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS), and Ultraviolet Photoemission Spectroscopy (UPS). With the combination of XPS, XAS and UPS methods, the absolute energies of the HOMO and LUMO can be determined for comparison to the valence and conduction band energies of the biosensitized semiconductor. The HOMO-LUMO gap of retinal was spectroscopically determined to be 2.49 eV. For comparison, we also test the feasibility of DFT calculations in determining the HOMO-LUMO gap of free retinal. Using the G-311G basis set, the calculated HOMO-LUMO gap was 2.69 eV. The results show that the DFT method overestimates the experimentally found band gap; consequently, higher level calculations are required.



#### 890-Pos

##### Photosynthetic Antenna Systems: The Place Where Light Interfaces with Biology

Robert E. Blankenship.

Washington Univ. In St. Louis, St. Louis, MO, USA.

All photosynthetic organisms contain a light-gathering antenna system, which functions to collect light and transfer energy to the reaction center complex where electron transfer reactions take place. Our work centers on the antenna complexes found in green photosynthetic bacteria, which include chlorosomes, the Fenna-Matthews-Olson (FMO) antenna protein and integral-membrane antenna and reaction center complexes. All of these complexes are involved in the light-energy collection process in these organisms, which are adapted for life in very low light intensities. Chlorosomes are ellipsoidal structures attached to the cytoplasmic side of the inner cell membrane. These antenna complexes provide a very large absorption cross section for light capture. Evidence is overwhelming that the chlorosome represents a very different type of antenna from that found in any other photosynthetic system yet studied. Chlorosomes do not con-

tain traditional pigment-proteins, in which the pigments bind to specific sites on proteins. These systems are of interest from both a basic science perspective of what is the structure of this unique class of photosynthetic antennas and how they work so efficiently, as well as more applied aspects in which the principles of self organization and extraordinary pigment properties that characterize these systems are used in a bio-mimetic approach to devise artificial light-energy capture systems. Recent work involves studies on the structure of the FMO antenna complex and the architecture of the membrane that includes the chlorosome, FMO protein and reaction center. Additional work involves using chlorosomes as part of bio-hybrid systems in which the biological complex feeds energy to an inorganic semiconductor substrate such as titanium dioxide.

#### 891-Pos

##### Investigating The CP29 Photosynthetic Light Harvesting Complex with 2D Electronic Spectroscopy

Naomi S. Ginsberg<sup>1,2</sup>, Jeffrey A. Davis<sup>3</sup>, Matteo Ballottari<sup>4</sup>,

Yuan-Chung Cheng<sup>5</sup>, Roberto Bassi<sup>4</sup>, Graham R. Fleming<sup>1,2</sup>.

<sup>1</sup>Lawrence Berkeley National Laboratory, Berkeley, CA, USA, <sup>2</sup>University of California at Berkeley, Berkeley, CA, USA, <sup>3</sup>Swinburne University of Technology, Melbourne, Australia, <sup>4</sup>University of Verona, Verona, Italy, <sup>5</sup>National Taiwan University, Taipei, Taiwan.

Though chlorophyll-binding protein CP29, a light harvesting complex in photosystem II of green plants, is proposed to play a role in the regulation of potentially-damaging excess chlorophyll excitations in the supercomplex, little is known about its spatial structure and its relation to excitation energy transfer dynamics and photoprotective action. *In vivo*, the presence of carotenoid pigment zeaxanthin is correlated with the quenching of excess chlorophyll excitations. Although the mechanism of quenching is still unknown, it is evident that CP29 exchanges carotenoid pigments depending on illumination conditions—in low light, the complex binds violaxanthin, while in high light zeaxanthin is bound.

We probe the chlorophyll Qy band of isolated CP29, binding either violaxanthin or zeaxanthin, using conventional and polarization-sensitive two-dimensional electronic spectroscopy (2DES) in order to better characterize electronic and spatial structure. 2DES resolves both excitation and emission energy of the molecular complexes being studied, providing a picture of the correlations between multiple excited states and revealing the presence of states that may go undetected by other spectroscopies. It also provides a direct map of excitation energy transfer processes within the complex by identifying signals from correlated donor and acceptor energies. Polarization-dependent studies provide clues in particular about chromophore configuration. We furthermore investigate whether the binding of zeaxanthin alters the excitation energy landscape and the resulting dynamics of CP29 to potentially modulate the quenching of excess excitations.

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#### 892-Pos

##### The Ligand Environment of the S<sub>2</sub> State of Photosystem II: A Study of the Hyperfine Interactions of the Tetranuclear Manganese Cluster by 2D Hyscore Spectroscopy.

K.V. Lakshmi, Sergey Milikisyan, Ruchira Chatterjee, Amanda M. Weyers, Ashley Meenaghan, Andrew Schwendeman, Christopher Coates.

Rensselaer Polytechnic Institute, Troy, NY, USA.

The solar water-splitting protein complex, photosystem II (PSII), catalyzes the light-driven oxidation of water to dioxygen in Nature. The four-electron water oxidation reaction occurs at the tetranuclear manganese-calcium-oxo (Mn<sub>4</sub>Ca-oxo) cluster that is present in the oxygen-evolving complex (OEC) of PSII. The mechanism of light-driven water oxidation has been a subject of intense interest and the OEC of PSII has been studied extensively by structural methods. While the recent X-ray crystal structures, single crystal EXAFS and EPR spectroscopy investigations provide a model for the geometry of the catalytic Mn<sub>4</sub>Ca-oxo cluster, there is limited knowledge of the protein environment that surrounds the catalytic site. It is suggested that the binding and activation of the substrate water molecules at the Mn<sub>4</sub>Ca-oxo cluster in the OEC of PSII are facilitated by key amino acid residues that could be ligated to the catalytic cluster. In this study, we demonstrate the application of two-dimensional (2D) hyperfine sub-level correlation spectroscopy to determine the magnetic couplings of the S<sub>2</sub> state of PSII. We utilize 2D difference spectroscopy to facilitate unambiguous assignments of the spectral features arising from the substrate molecules and surrounding amino acid residues in the S<sub>2</sub> state of PSII. The results presented here, for the first time, identify previously unknown ligands to the catalytic

cluster and provide avenues for the assignment of residues by site-directed mutagenesis and the refinement of computational and mechanistic models of PSII. <sup>®</sup> This study is supported by the Office of Basic Energy Sciences, United States Department of Energy (DE-FG02-0ER06-15).

### 893-Pos

#### Biochemical and Spectroscopic Analysis of Some Specific Cyanobacterial Species under Some Environmental Stress

Ashutosh Tripathi<sup>1</sup>, Shanthi Sundaram<sup>1</sup>, B.C. Tripathy<sup>2</sup>.

<sup>1</sup>University of Allahabad, Allahabad, Uttar Pradesh, India, <sup>2</sup>School of life sciences, JNU, New Delhi, India.

Sensor is a device which is used for the identification and estimation of an analyte. Several researches have shown the development of various types of sensors but an efficient, cost-effective and portable sensor is still required for the easy monitoring of water pollutants. PSII is the membrane protein complex found in oxygenic photosynthetic organisms which harnesses light energy to split H<sub>2</sub>O into O<sub>2</sub>, protons and electrons. A single celled cyanobacterial species is like chloroplast of higher plants. We have attempted using whole cells and permeabilised spheroplasts as a biosensing material for biosensor designing. We have observed the changes in their UV-Vis spectral properties, peak shifting, spectrofluorometric properties and oxygen evolution properties. The output results were available in a short time span. This property is most useful because its physiological activity can be easily monitored by amperometric/potentiometric systems. Such a biosensor will find application in the assessment of pollutants such as herbicides and heavy metals which affect electron transport in Z scheme of photosynthesis.

**Key Words:** Biosensor, PS- II particles, Cyanobacteria, Spectral Properties.

### 894-Pos

#### Excitation Dynamics of Light Harvesting Complex 2 B850 Ring

Johan Strumpher<sup>1,2</sup>, Klaus Schulten<sup>1,2</sup>.

<sup>1</sup>University of Illinois at Urbana-Champaign, Urbana, IL, USA, <sup>2</sup>Beckman Institute, Urbana, IL, USA.

The dynamics of excitation energy transfer within the B850 ring of light harvesting complex 2 from *Rhodobacter sphaeroides* and between neighboring B850 rings is investigated by means of the hierarchy equations of motion for dissipative quantum mechanics. The assumption of Boltzmann populated donor states for the calculation of inter-complex excitation transfer rates by generalized Förster theory is shown to give accurate results as intra-complex exciton relaxation occurs in about 1 ps. Utilizing generalized Förster theory, the primary channels of exciton transfer between B850 rings are found to be the five lowest-lying exciton states with the non-850 nm states making significant contributions to the total transfer rate.

### 895-Pos

#### Calculation of optical Properties from Molecular-Dynamics Simulations of Light-Harvesting Systems

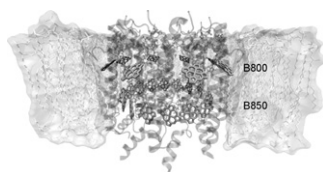
Carsten Olbrich, Jörg Liebers, Ulrich Kleinekathöfer.

Jacobs-University Bremen, Bremen, Germany.

Harvesting sun light to gain energy for life is initially done by light-harvesting antenna complexes containing chlorophyll and carotenoid molecules. Starting from the available crystal structure of the light-harvesting systems 2 (LH2) of purple bacterium, we applied all-atom classical molecular-dynamics (MD) simulations to the LH2 ring embedded in a membrane. Thus obtained thermal fluctuations of the nuclear positions provide the input for quantum chemical calculations. To obtain the energies of the Q<sub>y</sub> excited states of the single Bacteriochlorophyll (BChl) molecules, the semi-empirical ZINDO/CIS method is used to be able to analyze longer time series as was previously possible with the CIS method [1,2]. To include solvent effects to the excited state dynamics, the surrounding atoms of the BChls are treated as classical point charges in the QM calculations. Using the nuclear motion and the obtained energy differences between ground and Q<sub>y</sub> excited states with a time-dependent Hamiltonian, we are able to calculate optical properties of the analyzed system.

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### 896-Pos

#### Changes in Enthalpy of the Joliot-Kok Four Step Cycle to Produce Oxygen in Photosynthesis

David Mauzerall.

Rockefeller University, New York, NY, USA.

Changes in Enthalpy of the Joliot-Kok four-step cycle to produce oxygen in photosynthesis.

During photosynthesis, oxygen is produced from water in the four step Joliot-Kok cycle. The kinetics of this cycle have been extensively studied but the thermodynamics are still uncertain. An intriguing possibility is that evolution has found a path that allows a constant free energy difference for all the steps. This would strongly contrast with the sequential one-electron steps where the energies vary by over one electron-volt, or 100 kilojoules. Although the free energy or redox potentials of the intermediates are difficult to assess, the methodology of photoacoustics (PA) allows direct access to the enthalpy of the steps. Essentially the heat or enthalpy liberated by a photo-induced reaction causes an expansion of the media. The resulting sound wave is detected with a microphone. In certain leaves the oxygen itself produces a slower sound wave that can be used to verify the Joliot-Kok cycle of oxygen production. The PA measurement requires a weak pulse of light at the trap wavelength, 680 nm, to determine the enthalpy unalloyed with excess energy, interspersed with saturating pulses to advance the S-states of the Joliot-Kok cycle. A half dozen or more pulse pairs are required to obtain values for the four S-states. To enhance the signal to noise ratio, the cycle is then repeated following several minutes in the dark to allow the system to relax to the known state. The saturating flashes must be spaced by about 300 milliseconds to allow completion of the reaction but not allow decay of the S-states. Very preliminary results indicate that the differences in enthalpies of the reaction steps are small. This work was supported by the Rockefeller University.

### 897-Pos

#### Endor Spectrum of the Protonated Rhodosemiquinone in Bacterial Reaction Centers

Marco Flores<sup>1</sup>, Roger Isaacson<sup>2</sup>, Jennifer Shepherd<sup>3</sup>, Mark Paddock<sup>2</sup>, Melvin Okamura<sup>2</sup>.

<sup>1</sup>Arizona State University, Tempe, AZ, USA, <sup>2</sup>U of California, San Diego, La Jolla, CA, USA, <sup>3</sup>Gonzaga University, Spokane, WA, USA.

A crucial intermediate state in the reduction of Q<sub>B</sub> to Q<sub>B</sub>H<sub>2</sub> involves the high energy intermediate Q<sub>B</sub>H<sup>•</sup> state. (1) Direct observation of this state was achieved upon replacing the native ubiquinone with the low potential analog rhodosemiquinone (RQ). (2) Here we report the ENDOR spectrum of rhodosemiquinone at low and high pH measured in a mutant RC designed to reduce Q<sub>B</sub> via B-branch electron transfer without interference from Q<sub>A</sub><sup>•-</sup> (3, 4). The peaks at 50.2 MHz and 51.7 MHz (dashed lines) are shifted from the proton Larmor frequency (~53.2 MHz) and are assigned to hydrogen-bonded protons due to their line shape and position and their absence upon exchange in D<sub>2</sub>O (4). Upon shift to lower pH, these peaks diminish in amplitude and a new proton peak arises near 49.4 MHz (solid line). We attribute these changes to the protonation of rhodosemiquinone at lower pH. (Supported by NIH)

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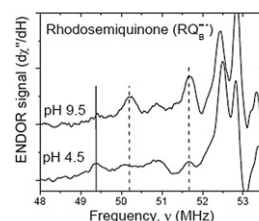


Figure. ENDOR spectrum of rhodosemiquinone in RC at low and high pH (ν=35 GHz, T=80K)

### 898-Pos

#### Novel Photosynthetic Reaction Center Chromophore Configuration

Brett Carter, Steven G. Boxer.

Stanford University, Stanford, CA, USA.

The *Rhodobacter capsulatus* reaction center mutant M204IQ appears to assemble without the bacteriochlorophyll B<sub>L</sub>, which serves as the electron acceptor or mediator of the primary charge separation reaction. Evidence supporting this conclusion to date includes the pigment ratio, low temperature absorption spectrum, steady-state fluorescence and absence of appreciable P<sup>+</sup>Q<sub>A</sub><sup>•-</sup> formation. If correct, this novel configuration of chromophores will enable many questions about the initial light driven electron transfer in RCs to be probed.

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