Title
THIRD SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE. JUNE 19-22, 1979 abstracts.

Author
Lawrence Berkeley National Laboratory

Publication Date
1979-06-28

THIRD SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE

June 19-22, 1979

Abstracts

Asilomar Conference Grounds
Pacific Grove, California

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

THIRD SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE

June 19-22, 1979

Abstracts

Asilomar Conference Grounds
Pacific Grove, California

Sponsored by
Basic Energy Sciences Division
U.S. Department of Energy

Contents

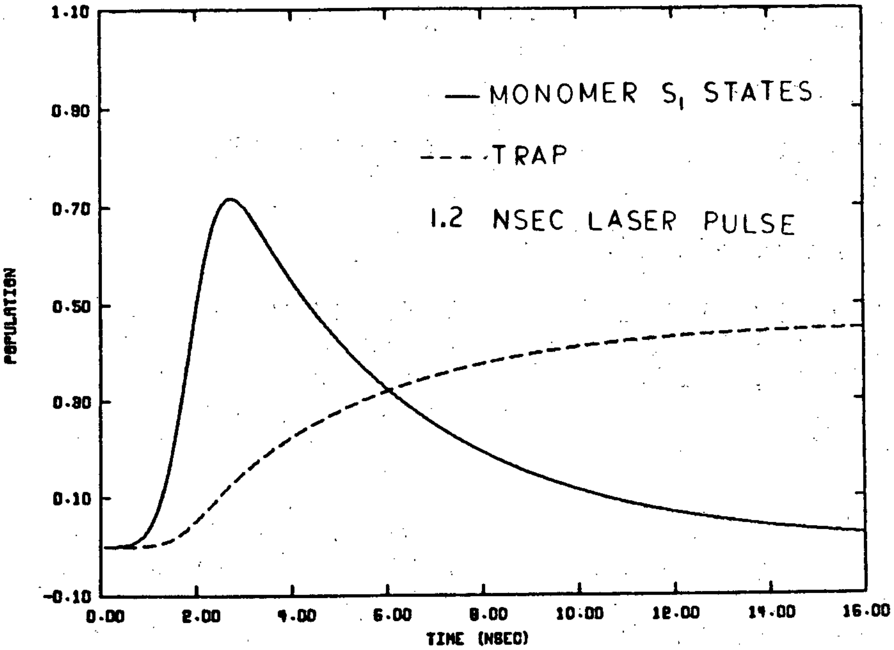
THEORETICAL STUDIES OF ENERGY TRANSFER

Lester L. Shipman

Chemistry Division

Argonne National Laboratory, Argonne, IL 60439

A system of computer codes has been developed for the investigation of the photodynamical behavior of chlorophyll (Chl) antennas coupled to phototraps. Included in the kinetics are the population of excited singlet states via laser pulses (e.g., 300 fsec, 20 psec, 1.2 nsec FWHM) or continuous illumination; unimolecular decay rates (i.e., intersystem crossing, internal conversion, fluorescence); Förster transfer of singlet excitation; and singlet excitation decay in the phototrap. A typical population and decay curve is shown below; the system consists of 0.04 M Chl a in pyridine with 2% of the Chl a molecules present as nonfluorescent phototraps.


2 PER CENT TRAPS, .04 M

The codes have been used to investigate concentration quenching of the fluorescence of Chl a and covalently-linked dimeric Chl a, fluorescence depolarization, and energy transfer and trapping by Chls embedded in membranes.

Publications

SPECTROSCOPIC CHARACTERIZATION OF THE PHEOPHYTIN a DICATION
W. Oettmeier, T. R. Janson, M. C. Thurnauer, L. L. Shipman and J. J. Katz
J. Phys. Chem. 81, 339-342 (1977)

CALCULATION OF THE ELECTRONIC SPECTRA OF CHLOROPHYLL a AND BACTERIOCHLOROPHYLL a-WATER ADDUCTS
L. L. Shipman and J. J. Katz
J. Phys. Chem. 81, 577-581 (1977)

PHOTOSYNTHESIS
J. J. Katz and L. L. Shipman
McGraw-Hill Yearbook of Science and Technology, New York, pp. 337-338, 1977.

OSCILLATOR AND DIPOLE STRENGTHS FOR CHLOROPHYLL AND RELATED MOLECULES
L. L. Shipman
Photochem. PHotobiol. 26, 287-292 (1977)

AB INITIO CALCULATIONS ON LARGE MOLECULES USING MOLECULAR FRAGMENTS. SCF-MO-CI STUDIES ON LOW-LYING SINGLET AND TRIPLET STATES OF PYRAZINE
J. D. Petke, R. E. Christoffersen, G. M. Maggiora and L. L. Shipman
Int. J. Quantum Chem.: Quantum Biol. Symp. 4, 343-355 (1977)

ANTENNA CHLOROPHYLL AND P700. EXCITON TRANSITIONS IN CHLOROPHYLL a ARRAYS
L. L. Shipman
J. Phys. Chem. 81, 2180-2184 (1977)

STEREOELECTRONIC PROPERTIES OF PHOTOSYNTHETIC AND RELATED SYSTEMS. 1. AB INITIO QUANTUM MECHANICAL GROUND STATE CHARACTERIZATION OF FREE BASE PORPHINE, CHLORIN, AND ETHYL PHEOPHORBIDE a
D. Spangler, G. M. Maggiora, L. L. Shipman and R. E. Christoffersen
J. Am. Chem. Soc. 99, 7470-7477 (1977)

STEREOELECTRONIC PROPERTIES OF PHOTOSYNTHETIC AND RELATED SYSTEMS. 2. AB INITIO QUANTUM MECHANICAL GROUND STATE CHARACTERIZATION OF MAGNESIUM PORPHINE, MAGNESIUM CHLORIN, AND ETHYL CHLOROPHYLLIDE a
D. Spangler, G. M. Maggiora, L. L. Shipman and R. E. Christoffersen
J. Am. Chem. Soc. 99, 7478-7489 (1977)

CHLOROPHYLL FUNCTION IN THE PHOTOSYNTHETIC REACTION CENTER
J. J. Katz, J. R. Norris, L. L. Shipman, M. C. Thurnauer, and M. R. Wasielewski
Ann. Rev. Biophys. Bioengin. 7, 393-434 (1978)

STEREOELECTRONIC PROPERTIES OF PHOTOSYNTHETIC AND RELATED SYSTEMS. AB INITIO CONFIGURATION INTERACTION CALCULATIONS ON THE GROUND AND LOWER EXCITED SINGLET AND TRIPLET STATES OF MAGNESIUM PORPHINE AND PORPHINE
J. D. Petke, G. M. Maggiora, L. L. Shipman and R. E. Christoffersen
J. Mol. Spec. 71, 64-84 (1978)

CHLOROPHYLL AGGREGATION: COORDINATION INTERACTIONS IN CHLOROPHYLL MONOMERS, DIMERS AND OLIGOMERS
J. J. Katz, L. L. Shipman, T. M. Cotton, and T. R. Janson
in The Porphyrins, D. Dolphin, Ed., Vol. V, Academic Press, New York, pp. 401-458 (1978)

STEREOELECTRONIC PROPERTIES OF PHOTOSYNTHETIC AND RELATED SYSTEMS. AB INITIO CONFIGURATION INTERACTION CALCULATIONS ON THE GROUND AND LOWER EXCITED SINGLET AND TRIPLET STATES OF MAGNESIUM CHLORIN AND CHLORIN
J. D. Petke, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen
J. Mol. Spec. 73, 311-331 (1978)

STRUCTURE AND FUNCTION OF PHOTOREACTION-CENTRE CHLOROPHYLL
J. J. Katz, L. L. Shipman and J. R. Norris
CIBA Foundation Symposium 61, Elsevier, NY, pp. 1-40, 1979

PRIMARY PROCESSES OF PHOTOSYNTHESIS. TOPICS IN PHOTOSYNTHESIS, A REVIEW
L. L. Shipman
Q. Rev. Biol. 53(4), 460 (1978)

FÖRSTER TRANSFER RATES FOR CHLOROPHYLL a
L. L. Shipman and David L. Housman
Photochem. Photobiol. IN PRESS

STEREOELECTRONIC PROPERTIES OF PHOTOSYNTHETIC AND RELATED SYSTEMS. V. AB INITIO CONFIGURATION INTERACTION CALCULATIONS ON THE GROUND AND LOWER EXCITED SINGLET AND TRIPLET STATES OF ETHYL CHLOROPHYLLIDE a AND ETHYL PHEOPHORBIDE a
J. D. Petke, G. M. Maggiora, L.L. Shipman and R. E. Christoffersen
Photochem. Photobiol. IN PRESS

RELAXED EXCITON STATES IN CHLOROPHYLL a ARRAYS
L. L. Shipman and Wendy A. Paster
J. Phys. Chem. Submitted (1979)

STEREOELECTRONIC PROPERTIES OF AGGREGATED CHLOROPHYLL SYSTEMS

Ralph E. Christoffersen and Gerald M. Maggiora
University of Kansas
Lawrence, Kansas 66045

The overall goal of our theoretical studies is to develop a detailed understanding of the molecular factors which contribute to the conversion of light energy into electrochemical energy in the photoreaction centers of plants and bacteria. To do this we have undertaken a series of detailed theoretical studies of the geometric and electronic structure and properties of isolated and aggregated chlorophyll systems.

Since our last report, substantial progress has been made towards this goal. In particular, ab initio self-consistent field configuration interaction (SCF CI) calculations have been completed on a number of molecules related to chlorophyll, such as chlorophyllide a, bacteriochlorophyllide a, and their corresponding free bases. These calculations explicitly include all macrocyclic ring substituents. Thus, possible electronic structural effects on the ground and excited states of the above molecules brought about by ring substituents can be assessed without resort to ad hoc approximations as is necessary in the π-electron procedures which have been applied until now. A variety of properties of the low-lying singlet and triplet states of these molecules have been examined, including state energies, singlet-singlet and triplet-triplet transition energies, oscillator strengths and polarizations, and electronic charge distributions. Earlier studies also examined the ground state of chlorophyllide systems. Calculated values of these properties compared very favorably with available experimental data, and also provided a number of insights into the electronic structural features of these systems not obtained in earlier experimental measurements. For example, a detailed analysis of the Soret band region in chlorophyllide a and bacteriochlorophyllide a indicates the presence of a large number of states, many of which possess significant contributions from doubly (and some higher) excited configurations. Earlier calculations which considered π-electrons and singly excited configurations only are incapable of providing such detailed data on this region of the singlet manifold. Our calculations also show that the $S_1 \leftarrow S_0$ transition in both chlorophyllide a and bacteriochlorophyllide a are clearly y-polarized.

Due to the importance of radical species in photosynthetic energy conversion, we have also extended our SCF CI calculations to include radical cation doublet states of the various chlorophyll systems studied above. Calculations have been completed on the ground and low-lying doublet states of chlorophyllide a and bacteriochlorophyllide a cation radicals. The calculated results show excellent agreement with available experimental data for doublet state energies, doublet-doublet transition energies, and relative oscillator strengths. Polarization data, which is not yet available experimentally, was also obtained as well as spin density distributions for the two lowest doublet states. The calculations also reveal a large number of states of very low oscillator strength spread across the entire spectral region of interest. Many of these states as well as those carrying measurable oscillator strength possess significant contributions from doubly and triply excited configurations. These results as well as those on neutral molecules point out clearly the need for extensive CI in the study of the excited states of chlorophyll systems. Studies are currently under way on the cation radicals of the free base species, and on assessing the feasibility of applying our approach to the corresponding anion radical systems.

The results from the above studies provide a clear indication of the feasibility of extending our studies to plant and bacterial "special-pair" dimers, and an analysis of the current theoretical and experimental situation on these special-pair systems has been presented.

We are pursuing two lines of investigation designed to characterize the geometric and electronic structure and properties of special-pair dimers. The first involves an assessment of the reliability of our current SCF CI procedures for the study of π-type dimer systems. We have chosen a series of cyclophane type systems (e.g., paracyclophanes, quinonophanes, and porphinophanes) for study since the geometric relationship of the interacting aromatic rings is particularly well-characterized in these systems due to the covalent linkages between the two rings. SCF CI studies are currently under way on the quinonophanes. An additional advantage gained by our studies on quinone systems is that they will provide a baseline for future studies on quinone systems of importance in photosynthesis.

The second line of investigation involves the development and characterization of a set of transferable empirical potential functions (EPF) suitable for studying the conformational energetics and properties of special-pair dimers. The intramolecular EPF's are tested by assessing their ability to provide reasonable values for a wide range of molecular properties such as bond angles, bond lengths, vibrational frequencies and intensities, mean square amplitudes of vibration, molecular enthalpies, and barriers to rotation. Our results to date are very encouraging, and we are currently in the process of investigating the reliability of our intermolecular EPF's using gas-phase data on aggregated systems and crystal packing analysis.

A summary of the above work will be presented with special emphasis being given to the results of the electronic structure studies along with a discussion of the applicability of the results to the study of oxidized and reduced special-pair dimers.

MANUSCRIPTS PUBLISHED, IN PRESS, OR SUBMITTED (Since January 1976)

1. "*Ab Initio* Calculations on Large Molecules Using Molecular Fragments. Comparison of Charge Distribution and Molecular Electrostatic Potential for Ethyl Chlorophyllide *a* and Related Molecules," T. Oie, G.M. Maggiora, and R.E. Christoffersen, *Int. J. Quantum Chem.*, *53*, 119-133 (1976).
2. "*Ab Initio* Calculations On Large Molecules Using Molecular Fragments. Generalization of Floating Spherical Gaussian Basis Sets," G.M. Maggiora and R.E. Christoffersen, *J. Amer. Chem. Soc.*, *98*, 8325-8332 (1976).
3. "Stereoelectronic Properties of Photosynthetic and Related Systems. I. Ground State Characterization of Free Base

Porphine, Chlorin, and Ethyl Pheophorbide a," D. Spangler, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen, J. Amer. Chem. Soc., 99, 7470-7477 (1977).

4. "Stereoelectronic Properties of Photosynthetic and Related Systems. II. Ground State Characterization of Magnesium Porphine, Magnesium Chlorin, and Ethyl Chlorophyllide a," D. Spangler, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen, J. Amer. Chem. Soc., 99, 7478-7489 (1977).

5. "Ab Initio Calculations On Large Molecules Using Molecular Fragments. SCF-MO-CI Studies on Low-Lying Singlet and Triplet States of Pyrazine," J.D. Petke, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen, Int. J. Quantum Chem., Quantum Biol. Symp., 4, 343-355 (1977).

6. "Stereoelectronic Properties of Monomeric and Aggregated Chlorophyll Systems," R.E. Christoffersen and Gerald M. Maggiora, Proceedings of 1st. ERDA Solar Photochemistry Research Conference, Argonne National Lab., 1977 (in press).

7. "Stereoelectronic Properties of Photosynthetic and Related Systems. III. Ab Initio Configuration Interaction Calculations on the Ground and Lower Excited Singlet and Triplet States of Magnesium Porphine and Porphine," J.D. Petke, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen, J. Molec. Spectr., 71, 64-84 (1978).

8. "Stereoelectronic Properties of Photosynthetic and Related Systems. IV. Ab Initio Configuration Interaction Calculations on the Ground and Lower Excited Singlet and Triplet States of Magnesium Chlorin and Chlorin," J.D. Petke, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen, J. Molec. Spectr., 73, 311-331 (1978).

9. "Development of Basis Sets for Molecular Calculations. A Comparison of Tetrahedral Gaussian Lobe Functions and Cartesian Gaussian Basis Sets," D. Spangler and R.E. Christoffersen, *Int. J. Quantum Chem.*: Quantum Bio. Symp. *5*, 127-135 (1978).

10. "Stereoelectronic Properties of Photosynthetic and Related Systems. V. *Ab Initio* Calculations on the Ground and Excited States of Chlorophyllide *a* and Pheophorbide *a*," J.D. Petke, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen, *Photochem. Photobio.* (in press).

11. "Electronic Structural Properties and Photosynthesis," R.E. Christoffersen, Proc. Kiev Conf. on Quantum Chemistry, Biology and Pharmacology, Kiev, USSR, 1978 (in press).

12. "An Assessment of Reaction Center Special-Pair Chlorophyll Models," G.M. Maggiora, Proc. Kiev Conf. on Quantum Chemistry, Biology, and Pharmacology, Kiev, USSR, 1978 (in press).

13. "*Ab Initio* Calculations on Large Molecules Using Molecular Fragments. Generalization of the Molecular Fragment Basis at the Minimum Basis Set Level," D. Spangler and R.E. Christoffersen, *Int. J. Quantum Chem.* (submitted).

14. "Stereoelectrinic Properties of Photosynthetic and Related Systems. VI. *Ab Initio* Calculations on the Ground and Excited States of Bacteriochlorophyllide *a* and Bacteriopheophytin *a*," J.D. Petke, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen (in preparation).

15. "Stereoelectrinic Properties of Photosynthetic and Related Systems. VII. *Ab Initio* Calculations on the Ground and Excited States of Chlorophyllide *a* and Bacteriochlorophyllide *a* Radical Cations," J.D. Petke, G.M. Maggiora, L.L. Shipman, and R.E. Christoffersen (in preparation).

EXTENDED HUCKEL CALCULATIONS ON PORPHYRINS, CHLORINS AND ISOBACTERIOCHLORINS:CORRELATION WITH OPTICAL AND MAGNETIC RESULTS

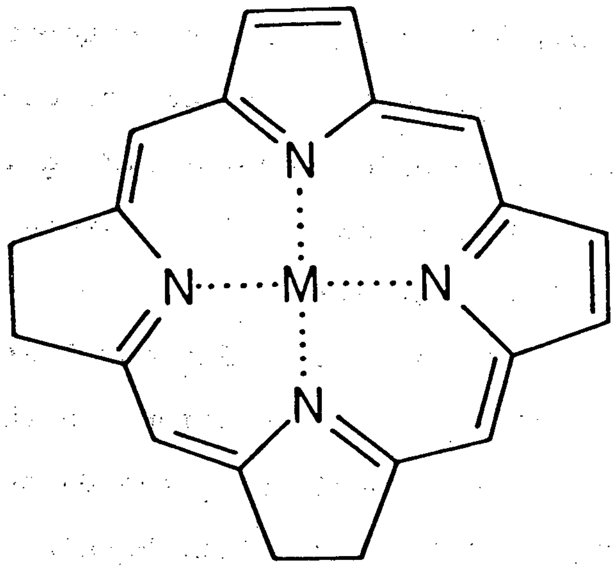
L. K. Hanson, P. F. Richardson and J. Fajer
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

Charge iterative extended Hückel calculations, which treat both π and σ electrons, have been used to guide and interpret work carried out on porphyrin transients involved in photosynthetic and metabolic processes. We describe here applications of these calculations to metalloisobacteriochlorins, radicals of chlorophyll and pheophytin, and oxygen interactions with manganese porphyrins.

1. Isobacteriochlorins.

Isobacteriochlorins (I) have recently elicited considerable interest because the prosthetic groups of sulfite and nitrite reductases have been shown to contain siroheme, an iron-isobacteriochlorin with eight carboxylic side chains. The enzymes catalyze the six-electron reduction of sulfite to hydrogen sulfide and of nitrite to ammonia. In green plants, the latter reaction $NO_2^- + 8H^+ + 6e \rightarrow NH_4^+ + 2H_2O$ is light driven: photosynthetically reduced pyridine dinucleotide serves as the electron donor for the reaction:

Chlorophyll → → NADH → flavoprotein → ferrodoxin → nitrite reductase.



I

A further biological role has more recently been attributed to isobacteriochlorins with the realization that sirohydrochlorins, demetallated sirohemes, are intermediates in the biosynthetic pathway of the corrin, vitamin B12. We have verified the structure of isobacteriochlorins, previously inferred from spectroscopic measurements, by x-ray diffraction of zinc tetraphenylisobacteriochlorin (ZnTPiBC). We are using this compound as a model of the siroheme to investigate the chemistry of this class of compounds and to separate the role of the ligand from that of the metal. ZnTPiBC is considerably easier to oxidize and harder to reduce than the corresponding porphyrin and chlorin. These redox properties may dictate the choice of the isobacteriochlorin skeleton in the reductase enzymes where the prosthetic group must mediate multiple electron transfer to the substrate. Electron spin resonance spectra have been obtained to map the electronic configuration of the radical. The unpaired spin density is largely localized at the two saturated rings of the isobacteriochlorin (8 protons, $a_H = 5.7$ G) with smaller densities found at the β protons of the other two pyrrole rings ($a_H = 0.8$ and 1.6 G) and at the nitrogens ($a_N = 0.9$ and 1.8 G) in agreement with the spin distribution predicted by the Hückel calculations. Calculations which treat sirohemes and the role of axial ligands are in progress.

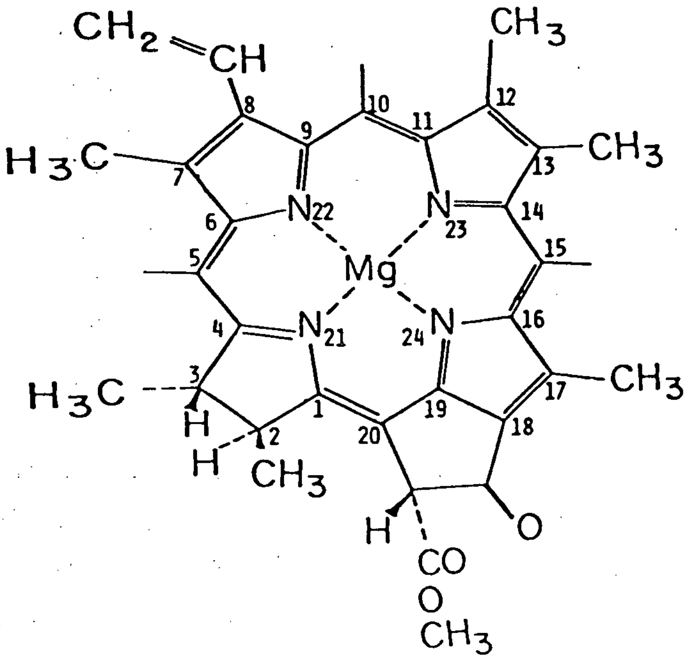
2. Chlorophylls, Pheophytins and Chlorins.

Extended Hückel calculations were carried out for anion and cation radicals of chlorins, chlorophyll and pheophytin. The calculations on the cations predict two nearly degenerate ground states $^2A_2$ and $^2B_2$ (C_{2v} symmetry) which are separated by $\sim$1000 cm^{-1} and exhibit significantly different spin densities. The spin density profiles of $Chl^{+\cdot}$ and metallochlorin cations have been extensively investigated (see Davis et al.) and are clearly consonant with the $^2A_2$ state predicted theoretically (Table 1). Particularly good agreement is found for the protons of ring IV, the methyl groups of rings I and III, and the nitrogens of $Chl^{+\cdot}$ which have been determined by selective deuteration, electron-nuclear double resonance and spin echo measurements (Katz, Norris et al.).

Chlorophyll and chlorin cations interact significantly with their environment as evidenced by their ESR and ENDOR spectra and by changes of their oxidation potentials as a function of temperature, solvent, and counterion (see Davis, et al.). These changes may reflect mixing of the two nearly degenerate ground

Table 1

EXTENDED HÜCKEL SPIN DENSITIES (ρ_π) FOR CHL A IN THE NORMAL "$^2A_2$" STATE AND THE EXCITED "$^2B_2$" STATE



POSITION	$\rho_\pi(^2A_2)$	$\rho_\pi(^2B_2)$
1	0.065	0.008
4	0.075	0.001
5	0.063	0.099
6	0.042	0.001
7	0.017	0.001
8	0.009	0.001
9	0.059	0.000
10	0.027	0.089
11	0.050	0.001
12	0.024	0.002
13	0.006	0.002
14	0.063	0.001
15	0.008	0.070
16	0.063	0.000
17	0.042	0.001
18	0.014	0.000
19	0.061	0.001
20	0.006	0.080
21(N)	0.006	0.106
22(N)	0.055	0.112
23(N)	0.008	0.088
24(N)	0.002	0.082
25	0.001	0.000
26	0.006	0.000
27	0.000	0.000
28(O)	0.029	0.019

states predicted theoretically. The $^2B_2$ "excited" state shows significantly smaller spin densities at the α-carbon of the saturated ring than the $^2A_2$ state. If the solvent or counterion induce a sufficient perturbation to mix in some character of the excited state, then the splitting constants of the β protons would result in lower values than expected for a pure $^2A_2$. The Hückel calculations actually predict that ligands such as H_2O, CH_3OH, CH_3SH, CH_3CN and THF would suppress the excited state below the $^2A_2$ in chlorins and chlorophyll. Although this is not observed experimentally, the calculations clearly suggest that interactions between the two states are energetically accessible. Changes in the coordination sphere of the chlorins provide a likely mechanism for this mixing.

Extrapolation of these results to P680, the primary donor of Photosystem II, has led to the proposal that P680 is a monomeric Chl, whose coordination sphere (possibly by protein residues), controls its function as the phototrap of Photosystem II via a mixing of the two states we have described.

The anions of Chl and pheophytin (Pheo) are under consideration as the primary acceptors of Photosystems I and II. Comparison of the ESR and ENDOR results recently obtained for anions of Chl, Pheo and chlorins again show good agreement with extended Hückel calculations for these species.

The combination of experimental and theoretical results thus help define the electronic profile of the primary acceptor and donor species of plant photosynthesis.

3. Griffith Model Bonding in Oxygen-Manganese Complexes.

As an additional example of the usefulness of Hückel calculations in treating axial ligand effects, we consider here the interaction of manganese porphyrins with oxygen. Mn(II) porphyrins bind O_2 reversibly at $-80^\circ C$ in organic solvents to form pentacoordinated complexes, in contrast to the hexacoordinated O_2 complexes formed by iron and cobalt porphyrins. The reaction with O_2 transforms the Mn(II) porphyrin spectrum from the normal to "hyper" type with a split Soret band typical of Mn(III) porphyrins. EPR spectra indicate a spin change from $S = 5/2$ to $S = 3/2$ and ^{17}O substitution indicates little unpaired spin density on the O_2. Analysis of the EPR data[1] suggested that the O_2 molecule binds to the Mn in the Griffith mode (edge-on, parallel to the porphyrin plane) and

---

[1] B. M. Hoffman, et al., JACS 98, 5473 (1976).

that the complexes could be formally described as Mn(IV)$O_2^{=}$. However, published ab initio calculations[2] predicted instead that Mn(III)O_2^- should be the most stable configuration, with O_2 bound in the Pauling mode (end-on, bent). Hückel calculations were carried out for both the Griffith and Pauling models for O_2·Mn porphins, in which the O–O, Mn–O, out of plane Mn distances and the O–O orientation above the porphinato plane were varied. All of the experimental results can be explained in terms of the Griffith model but not the Pauling model. Furthermore, our calculations suggest that the ab initio results may be due to the use of an incorrect geometry. We conclude therefore that, unlike Co(II) and Fe(II) porphyrins, Mn(II) porphyrins bind oxygen in the Griffith mode in a manner similar to that found for Ti porphyrins.

Relevant Publications:

1. Molecular Orbital Calculations of Chlorophylls and Chlorins, L. K. Hanson, M. S. Davis, I. Fujita and J. Fajer, Biophys. J. 21, 195a (1978).
2. Griffith Model Binding in Oxygen-Manganese Porphyrin Complexes, L. K. Hanson and B. M. Hoffman, Biophys. J. 25, 185a (1979).
3. Axial Ligand Effects on Iron and Manganese Porphyrins: Extended Huckel Calculations of Cytochrome 450 Analogs and of O_2 Binding to Iron and Manganese, L. K. Hanson, submitted to Intern. J. Quantum Chem.

---

[2] A. Dedieu, et al., JACS 99, 8050 (1977).

Structural Features of Chlorophyll Complexes In Vitro and In Vivo As Determined By Triplet State ODMR

Richard H. Clarke

Department of Chemistry, Boston University
Boston, MA 02215

The photoexcited triplet state of the chlorophyll molecule has been the subject of extensive investigation by a variety of EPR techniques in recent years. The zero-field splittings have been reported for the commonly occuring forms of the chlorophyll and bacteriochlorophyll molecules, as well as most of the important derivative structures. In addition, intersystem crossing rates have been measured for the individual triplet state spin sublevels of many of these chlorophylls. There has emerged from these efforts a fairly comprehensive description of the electron distribution in the chlorophyll triplet state and the mechanisms active in promoting intersystem crossing in the chlorophyll molecule. In our recent work we have suggested that the triplet zero-field splitting and intersystem crossing rates could be utilized to provide structural information in chlorophyll aggregates. Specifically, the structure of a chlorophyll dimer such as might exist in the reaction center "special pair" could be inferred from the triplet properties as interpreted within the framework of a simple triplet exciton treatment. If the assumptions of the triplet exciton approach, as applied successfully in the description of triplet exciton states in organic molecular solids are applicable to the chlorophyll aggregate, then both the values of the zero-field splittings and the intersystem crossing rate constants in the chlorophyll dimer are expected to be directly dependent on the relative orientation of the chlorophyll molecules in the pair. We have used this approach to investigate the makeup of chlorophyll aggregates in vitro and in vivo.

The ability to investigate the structural aspects of specific chlorophyll aggregate units within a given sample by triplet state EPR is dependent on the ability to select and isolate the unit of interest from what may be a complex system. This is particularly important when several forms of the chlorophyll aggregate may exist simultaneously, as in a solution containing equilibrium mixtures of monomer, dimer, and higher aggregates, or in vivo, where several chlorophyll aggregate forms are expected in the reaction centers and antenna systems. In such cases optically detected magnetic resonance (ODMR), as developed in our laboratory for application to chlorophylls, allows an optical screening of the system, monitoring the triplet state EPR spectrum on fluorescence peaks which originate from the unit of interest. And by varying the optical detection wavelength among the fluorescence peaks, structural features from different chlorophyll units within the same sample may be evaluated and compared under identical conditions.

We have investigated the photoexcited triplet state zero-field splittings, overall triplet lifetimes and individual spin sublevel intersystem crossing rate constants at 2K for chlorophyll aggregates in organic solvents and for naturally occuring chlor ophyll aggregates extracted from green plants, using ODMR spectroscopy. Work on the in vitro chlorophyll aggregates allowed an assesment of the applicability of the triplet exciton model for structural evaluation of chlorophyll systems and serves as a basis for interpretation of ODMR spectra obtained for in vivo chlorophyll units. These data will be discussed in terms of the current models for chlorophyll reaction center and antenna structure and the possible conformation of in vivo chlorophyll aggregates in green plants.

Publications:

R. H. Clarke, D. R. Hobart, and W. R. Leenstra
J. Am. Chem. Soc., <u>101</u>, xxxx (1979) (April 25 issue)

R. H. Clarke, D. R. Hobart, and W. R. Leenstra
Semicond. Insul., <u>4</u>, 313 (1978)

R. H. Clarke, R. E. Connors and H. A. Frank
Proc. Third Intl. Conf. Energy Transfer in Condensed Matter, J. Fiala, ed.
Charles University Press, Prague, 1978. P. 67

R. H. Clarke and D. R. Hobart
FEBS Letters, <u>82</u>, 155 (1977)

R. H. Clarke and H. A. Frank
Chem. Phys. Lett., <u>51</u>, 13 (1977)

R. H. Clarke, R. E. Connors, H. A. Frank, and J. C. Hoch
Chem. Phys. Lett., <u>50</u>, 61 (1977)

Excited State Properties of Models for Reaction Center Chlorophyll

by

K. J. Kaufmann, Department of Chemistry, University of Illinois, and M. J. Pellin and M. R. Wasielewski, Chemistry Division, Argonne National Laboratory.

The primary role of chlorophyll (Chl) in photosynthetic organisms is to convert incident solar radiation into chemical energy. Photons are captured by an extended array of Chl molecules known as the antenna. The electronic excitation produced by the light absorption is transmitted via the antenna Chl to a "special pair" of chlorophyll molecules. This pair of molecules traps the excitation energy and then rapidly undergoes one electron oxidation. The resulting charge separation subsequently generates a chemical potential gradient within the organism. The special pair and its associated redox components are contained in a protein matrix and are collectively known as the reaction center. Although reaction centers of Photosystem I (P700) in green plants have not as yet been isolated completely free of antenna, a great deal of information exists regarding their spectroscopic properties. P700 undergoes bleaching upon illumination with 700 nm light. The subsequent appearance of a photoinduced electron spin resonance (esr) signal of about 7 gauss linewidth with g = 2.0025 results from the formation $P700^{\dot{+}}$. A comparison between the signal of monomeric Chl $a^{\dot{+}}$ and $P700^{\dot{+}}$ reveals that the linewidth of the signal due to the in vivo species is narrower by $\sqrt{2}$ than that of in vitro Chl $a^{\dot{+}}$. This result agrees with a theoretical prediction for the linewidth resulting from a one electron spin delocalized equally over two Chl molecules.

The finding that two Chl molecules closely interact in vivo to form P700 has stimulated efforts to prepare an in vitro chlorophyll special pair

(Chl_{sp}). Chl a adducts with ehtanol have been prepared that successfully mimic the optical and esr properties of photosystem I reaction center chlorophyll. These Chl_{sp} systems are assembled from two monomer units by cooling a mixture of Chl a and ethanol (or H_2O) in hydrocarbon solvents to below 100K. Covalently linked dimers of both Chl a and pyrochlorophyll a (PChl a) have been prepared which also reproduce the spectroscopic and redox properties of P700. The two chlorophylls are joined in each case at their propionic acid side chains via an ethylene glycol diester linkage. The orientation of the chlorophyll macrocycles with respect to one another and consequently their electronic properties depend strongly on the solvation conditions. Treating solutions of these covalent dimers in dry non-nucleophilic solvents, e.g., toluene, CCl_4, CH_2Cl_2 with 10-100 fold molar excesses of a hydrogen bonding nucleophile (e.g., ROH) results in their folding into the C_2 symmetric conformation depicted below. This folding is accompanied by shifts of both their longest wavelength absorption band (663 nm to 694 nm) and in their fluorescence maxima (670 nm to 735 nm).[17-18] By studying the properties of a model for the P700 special pair we hoped to gain insight into the primary photosynthetic events.

The pyrochlorophyll dimer was studied using time resolved absorption and time resolved fluorescence spectroscopy. Two salient features were observed in the fluorescence lifetime measurements. At 298K, the lifetime of the dimer was strongly dependent on the solvent being 3.8 nsec in CCl_4, 1.5 nsec in $CHCl_3$ and 110 psec in CH_2Cl_2. The fluorescence lifetime in CH_2Cl_2 varied by more than a factor of 20 between 298K and 200K, yet the fluorescence quantum yield was insensitive to temperature. Excited state absorption studies revealed the presence of two excited singlet states. The difference spectrum of one of these states had a bleaching at 700 nm.

The observation of these two states depended strongly on the nature of the solvent and the temperature.

Analysis of the data in terms of a model for the excited state of the model for Chl_{sp} indicates that there are two singlet excited states. The relative populations of these states is controlled not by thermodynamics as is usually the case for excited states within the singlet manifold, but but by kinetics. The dependence of the rate constant for transition from one state to the other is strongly dependent on the solvent and temperature and accounts for the observed behavior of the dimer. This two-state model may have important consequences for photosynthesis. It provides a means by which the plant can briefly store energy, while waiting for an acceptor to become oxidized or if necessary to quickly dispose of the excitation energy if the redox chain is occupied. Such an effect may have already been observed by others in <u>Rps viridis</u>. Reduction of the first acceptor prior to illumination results in a singlet lifetime for the bacteriochlorophyll special pair of only 20 picoseconds. This is in contrast to an expected lifetime of several nanoseconds based on estimates of the radiative lifetime obtained from the absorption spectrum. Since we have found the relaxation of the singlet excited state is very sensitive to the environment, the presence of the reduced acceptor might be enough of a perturbation to favor the same short lived excited singlet state we have reported for the Chl_{sp} in vitro.

<u>Recent Publications Related to this Work</u>

1. Modulation of the Primary Electron Transfer Rate in Photosynthetic Reaction Centers by Reduction of a Secondary Acceptor, M. J. Pellin, C. A. Wraight and K. J. Kaufmann, Biophys. J. <u>78</u>, 361 (1979).
2. Picosecond Spectroscopy Applied to the Study of Chemical and Biological Systems, K. J. Kaufmann, CRC Solid State Reviews, February, 1979, pp. 265-316.
3. Applications of Video Detection to Picosecond Spectroscopy, K. J. Kaufmann, K. K. Smith and C. J. Hawley, Proceedings SPIE <u>48</u>, 124 (1978).
4. In vitro Duplication of the Primary Light-induced Charge Separation in Purple Photosynthetic Bacteria, Michael J. Pellin, Kenneth J. Kaufmann and Michael R. Wasielewski, Nature <u>278</u>, 54 (1979).

5. Picosecond Photophysics of Covalently Linked Pyro-Chlorophyllide a Dimer. Unique Kinetics Within the Singlet Manifold, submitted for publication.

6. Primary Photochemistry of the Reaction Center of Photosystem I, J. M. Fenton, M. J. Pellin, Govindjee, and K. J. Kaufmann, FEBS Lett., In press.

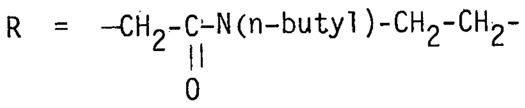
Singlet State Charge Transfer Reactions in Cofacial Diporphyrins[1]

C. K. Chang,† J. Fajer,† I. Fujita,† P. Kroger,* and T. L. Netzel*

Department of Energy and Environment† and
Department of Chemistry*
Brookhaven National Laboratory
Upton, NY 11973

Stacked double-macrocyclic or cofacial diporphyrin (CDP) molecules were investigated for their ability to transfer charge from their first excited singlet state. Several systems at room temperature were examined with the techniques of picosecond absorption spectroscopy. The excited state spectra in the 550 to 850 nm region were measured after photolysis with a 527 nm pulse of 6 ps duration (FWHM).

The CDP's studied were comprised of two porphyrin monomers held rigidly in place with two covalently bound side chains (R).



$$R = -CH_2-\underset{\underset{O}{\|}}{C}-N(\text{n-butyl})-CH_2-CH_2-$$

The center-to-center inter-ring distance was 4.2 ± 0.3 Å. Three CDP's were studied: H_2-H_2, two free-base units; Mg-H_2, one Mg-porphyrin and one free-base unit; and Mg-Mg, two Mg-porphyrins.

The goal of this work was to contrast CDP singlet state behavior with that of bimolecular porphyrin electron transfer reactions and that of natural photosynthetic systems. Chlorophylls, pheophytins and porphyrins are known to transfer charge readily from their lowest triplet states. However, only a few percent yield of charge transfer (CT) products have been found for singlet state reactants. In contrast, reactions (1) and (2) have been found to occur in photoexcited reaction centers isolated from photosynthetic bacteria.[2]

$$(BChl)_2^S\ Bph(Q^{\bar{\cdot}}Fe) \xrightarrow{<10\ ps} (BChl)_2^{\overset{+}{\cdot}}\ Bph^{\bar{\cdot}}(Q^{\bar{\cdot}}Fe) \qquad (1)$$

The yield of (1) is ∿100 percent. Importantly, the dark decay reaction (2) is slow.

$$(BChl)_2^{\overset{+}{\cdot}}\ Bph^{\bar{\cdot}}(Q^{\bar{\cdot}}Fe) \xrightarrow{\sim 10\ ns} (BChl)_2\ Bph(Q^{\bar{\cdot}}Fe) \qquad (2)$$

For all three CDP's in THF, only singlet to triplet state behavior was found ($K > \sim 2 \times 10^8\ s^{-1}$). When the solvent was changed to CH_2Cl_2 a completely new transient absorption spectrum at $t = 0 \pm 4$ ps was observed for the Mg-H_2 diporphyrin. It was much more peaked and absorbed more strongly than the corresponding singlet in THF. The λ_{max} at 660 nm agreed well with the expected absorptions of a Mg-$OEP^{\overset{+}{\cdot}}$ and H_2-$OEP^{\bar{\cdot}}$ (OEP = octaethylporphin) type of CT product. It decayed in 380 ± 40 ps to a long lived triplet state. When 0.1 M Et_4NCl was added to Mg-H_2 in CH_2Cl_2, the same CT state was found again. Now, however, it decayed in 620 ± 20 ps directly to the ground state.

These results can be analyzed in terms of a scheme closely modeled after one described by Seeley.[3] The purpose is to relate spectroscopic and electrochemical measurements to establish necessary conditions for $S_1 \rightarrow CT$ reactions. The chief virtue of this analysis is that it focuses consideration on the molecular interactions controlling these reactions. Presently available expressions for calculating ion-solvent interactions are rough approximations, but they can be used as guides for designing efficient light harvesting molecules.

A diporphyrin system, such as Mg-H_2, has a geometrical advantage over a bimolecular CT reaction. This is, for the bimolecular case donor and acceptor collisions can occur with a great variety of orientations. Only a few of these may be effective in producing a CT product. This can make the CT reaction an inefficient competitor to intersystem crossing. Current CDP studies are examining the effect of chain length and relative orientation on the probability of producing a CT product and on controlling its lifetime.

Footnotes

1. This work was carried out under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.
2. $(BChl)_2^S$ is a Bacteriochlorophyll-*a* dimer singlet state; Bph is a Bachteriopheophytin-*a* molecule; and $(Q^{\bar{\cdot}}Fe)$ is a quinone molecule in association with a non-heme iron that is maintained in a reduced condition.
3. G. R. Seeley, Photochem. Photobiol. (1978) *27*, 639-654.

Recent Publications

Early events and transient chemistry in the photohomolysis of alkyl-cobalamins, J. F. Endicott and T. L. Netzel, J. Am. Chem. Soc. (submitted).

Cofacial diporphyrin charge transfer reactions, C. K. Chang, J. Fajer, I. Fujita, P. Kroger, and T. L. Netzel (in preparation).

I - THE EFFICIENCY OF PHOTO-REDOX REACTIONS IN SOLUTION
II - PHOTOPROCESSES IN CHLOROPHYLL AGGREGATES

Henry Linschitz
Dept. of Chemistry, Brandeis University
Waltham, Mass. 02154

I - Photo-Redox Reactions in Solution - Photosynthesis and related processes for conversion of light into chemical or electrical energy confront the general problem of dissipative side-reactions. In the case of photo-redox processes leading to a radical pair, energy dissipation may occur in the initial reaction complex (quenching) or via back-reactions prior to stabilization of the high-energy products. To help guide development of systems designed to avoid these losses, we are studying competitive quenching and radical separation processes in solution. As test reactions we have been using photo-reduction of ketones and photo-oxidation of porphyrins. The rates of excited state (triplet) redox reactions and the yields of separated radicals or radical-ions are measured by laser-flash photolysis techniques. Methods have been developed for determining radical yields even when extinction co-efficients are not initially available.

In both ketone and porphyrin redox systems, it is found that decreasing the solvent polarity from acetonitrile to benzene changes the radical yield from essentially unity to zero, with relatively minor changes in the rate of (triplet) interaction. A similar drop in yield is found (for the triplet fluorenone-DABCO reaction) when the diffusion parameter, $T^{1/2}/\eta$ is decreased. In the transition region where this drop occurs, rather weak ($\sim$500 Gauss) magnetic fields partially restore the radical yield. Singlet excited states, reacting with the same redox reagents, give much lower yields than triplets.

These results are in accord with an intuitively simple picture of the reaction. This involves initial formation of a more-or-less polar excited reaction complex, charge transfer within this complex and escape of radical-ions from the cage within a time limit imposed by the competing radiationless conversion to the ground state. This time is much longer for triplet than for singlet pairs, emphasizing the problem of understanding high redox yields from singlet chlorophyll in vivo.

II - Photoprocesses in Chlorophyll Aggregates - Models of the 695 nm "reaction center" of photosynthesis have been prepared by covalently linking pyrochlorophyll units, or by inducing chlorophyll association by controlling the temperature and solvent. Flash excitation leads to "opening" of the dimer and formation of a triplet - ground state pair. Refolding can be directly observed.

Studies on "dry" chlorophyll-a solutions, using such activators as "Eu(fod)$_3$" or hexafluoro-isopropanol, demonstrate a specific, weak fluorescence at 678 nm, corresponding to absorption at 450 nm and assignable to a "donor state" of chlorophyll.

Work planned for the future involves extension of the program on radical yields to other variables, including strong electric fields, redox potentials and specifically structured solvent cages. Experiments on heterogeneous systems and photo-redox studies on chlorophyll dimers will also be undertaken.

Recent Publications:

1 - "Anion and Solvent Effects on the Rate of Reduction of Triplet Excited Thiazine Dyes by Ferrous Ions", P.D.Wildes, N. Lichtin, M.Z.Hoffman, L.J.Andrews and H.Linschitz, Photochem and Photobiol., 25. 21 (1977)

2 - "Kinetic Analysis of Flash Photolysis Data for Sequential First and Second Order Kinetics", L.J.Andrews, J.M.Levy and H.Linschitz, J. Photochem, 6, 355 (1977)

3 - "Photophysical Processes in Fluorenone", L.J.Andrews, A. Deroulede and H. Linschitz, J. Phys. Chem. 82, 2304 (1978)

4 - "Photoprocesses in Covalently Linked Pyrochlorophyllide Dimer", N. Periasamy, H. Linschitz, G. L.Closs and S.G.Boxer, Proc. Nat'l. Acad. Sci. USA, 75, 2563 (1978)

5 - "Photodisaggregation of Chlorophyll a and b Dimers", N. Periasamy and H. Linschitz, J. Am. Chem. Soc., 101, 1056 (1979)

6 - "Competing Cage Escape and Spin Rephasing Processes: Temperature - Viscosity and Magnetic Field Effects in the Photoreduction of Fluorenone by DABCO", N. Periasamy and H. Linschitz, Chem. Phys. Lett., in press.

MULTIPHOTON REDOX PHOTOCHEMISTRY

John S. Connolly, James C. Smart and Arthur J. Frank
Solar Energy Research Institute*
Golden, Colorado

Introduction

Utilization of solar energy to generate fuels and chemicals from abundant and renewable resources will make a significant impact on future world energy supplies. Our long-term goals are directed toward photoreduction of carbon dioxide to methanol and methane and of molecular nitrogen to ammonia. In the process, however, it is necessary to understand somewhat simpler processes, and our shorter term goal is to achieve photochemical splitting of water using visible light. All of the above reactions can be driven, in principle, with light in the 610 to 670 nm region.

The key elements of our research program at SERI are:

- calculations of optimal solar efficiencies of multiphoton processes;
- photophysical and photochemical studies of sensitizers;
- synthesis and characterization of redox catalysts and coupling to photosensitizers; and
- incorporation of coupled systems into molecular assemblies.

Each of these is discussed in turn in the following sections.

Solar Efficiencies of Multiphoton Processes

Bolton [1] has calculated the theoretical solar efficiencies of photochemical processes utilizing one, two and three photons. For two photons, the optimally efficient combination of solar wavelengths is 730 and 1320 nm, for which the calculated ideal efficiency is $\sim$44%. In contrast, the efficiency of a single photon of the same total energy (2.64 eV, 470 nm) is only about 11%. Similarly, the optimum wavelength combination of three photons is 570, 820 and 1330 nm which yields a calculated efficiency of about 50%. We are extending Bolton's calculations for four-, six- and eight-photon processes. For $n \geq 4$, the calculations of optimal wavelengths are more cumbersome, but our results to date indicate that the incremental increase in theoretical

---

* A Division of Midwest Research Institute. Operated for the Department of Energy under Contract EG-77-C-01-4042.

solar efficiency for each additional photon converges rapidly for n > 3 to about 60%. We shall present the results of calculations in the context of water splitting (n = 4), nitrogen fixation (n = 6) and reduction of carbon dioxide (n = 8).

Photosensitizers

For reasons discussed previously [2, 3], we consider bacteriochlorophyll a (BChl a) a model photosensitizer. Briefly, the available experimental evidence [4] indicates that the lowest triplet energy of this pigment is less than half the singlet excitation energy, and that electron transfer between triplets is an energetically favorable process.

Current investigations are focused on a search for evidence of charge-transfer quenching in the highly efficient triplet-triplet annihilation process. Specifically, we have undertaken laser flash photolysis studies [5] employing a fast infrared dectector in order to examine the 900 to 950 nm region where both the radical-cation and radical-anion have significant absorption [6, 7]. Solvent systems include pyridine, ethanol, acetonitrile and aqueous micelles (SDS). As of this writing, the IR photodiode has just been installed and the detailed spectral studies are yet to be carried out. However, several interesting effects have been observed in the aqueous micelles. Of particular interest is our observation of two, and perhaps three, laser-induced transient species in BChl a dissolved in SDS at ~10 times the critical micelle concentration. The decay kinetics appear to be first-order with well-separated lifetimes; spectra taken at 20-40 nsec and 400 nsec after the laser pulse are closely similar and differ only in magnitude. These investigations are being continued.

Synthesis and Characterization of Redox Catalysts

Coordinatively unsaturated metallocene derivatives of early transition metals have been particularly important in homogenous reduction, both stoichiometric and catalytic, of substrates such as N_2, CO, CO_2, olefins and acetylenes to yield reduced, hydrogenated and coupled products. We are pursuing synthetic and reaction studies of a class of dinuclear complexes containing the bridging fulvalene ligand [8]. The results indicate that metallofulvalene complexes can exist in a much wider range of oxidation states than the parent metallocenes [9], and that metal-metal bonding and coordination of small molecules between metal centers is a prominent feature of these complexes. This indicates that these complexes are ideal candidates for both multielectron storage and activation and reduction of small molecules.

We have also observed [10] that both electron-rich and electron-deficient metallofulvalene complexes exhibit intense absorption bands in the visible to near IR region that overlap quite well with the solar spectrum. These low-energy transitions are characteristic of the dinuclear metallofulvalene structures and are absent in the parent metallocenes and ring-substituted derivatives.

The combined features of this class of compounds, together with our ability to systematically vary the nature of the bridging ligand as well as the geometry and electronic structures of a wide variety of transition metal derivatives, indicate that these systems are ideal candidates for consideration as photoredox systems, by both direct and sensitized processes. This program of specific synthesis and characterization will include detailed investigations of their photophysical, photochemical and electrochemical properties.

Initially, we are concentrating on compounds related to bis (fulvalene) dimetal complexes containing cobalt and vanadium moieties. In addition, we shall investigate other organometallic systems including coordination complexes with delocalized ligands, metal-cluster compounds and molecules containing both organic dyes and coordinatively unsaturated metal centers.

Coupled Systems in Molecular Assemblies

In the last few years, several important advances in photochemical solar energy conversion have taken place. Several research groups [11] have reduced water to molecular hydrogen using visible light. Similarly, Creutz and Sutin [12], and later Harriman and Porter [13], reported evolution of oxygen from water using visible light. In each of these systems, an irreversible redox couple was required either to generate or to consume the transferred electrons. In order to couple the hydrogen- and oxygen-producing systems, some means must be developed to prevent the back reaction between the labile, primary charge carriers. One method of inhibiting reverse electron transfer is to select redox systems in which the back reaction, although thermodynamically favored, is kinetically slow. The basis for such a selection is a salient feature of the electron-transfer theory of Marcus [14] for which there is a growing body of experimental support [15]. Another alternative is to search for redox systems in which the labile intermediates formed in the forward reaction are converted to stable products before geminate recombination of the primary charges can occur.

A third method to suppress back electron transfer is to use membranes. The advantages of this approach over other alternatives include:

- the possibility of accomodating chemical species with markedly different solubilities, thus making available a wider range of reversible redox couples;
- the ability to separate stable chemical end-products;
- the possibility of ordering and orienting molecular systems in the membrane to facilitate both charge- and energy-transfer; and
- the possibility of varying the distance between reaction components in order to promote one conversion mechanism over another (charge- vs. energy-transfer) and also to enhance the efficiency of quantum utilization. For example, by placing the light-absorbing species and its reaction partner in close proximity, the excited singlet state rather than the triplet state may be used to drive a redox reaction, thus precluding loss of the singlet-triplet energy [16].

Overcoming these difficulties, particularly the last two, rests on our ability to answer some fundamental questions on electron- and energy-transfer and to manipulate the molecular architecture by specific synthesis. Exploration of these factors in the water-splitting reaction will form the basis of this aspect of our research program.

Acknowledgments

One of us (JSC) would like to thank Professor Henry Linschitz for his generous hospitality during frequent visits to Brandeis University where the laser flash photolysis and micelle studies were conducted. The bacteriochlorophyll was a gift from Dr. Joseph J. Katz, Chemistry Division, Argonne National Laboratory.

References

1. J. R. Bolton, Science 202, 705 (1978).
2. J. S. Connolly, Abstract, First Int. Conf. Photochem. Conv. Stor. Solar Energy, London, Ontario, July 1976.
3. J. S. Connolly, Abstract, Second Int. Conf. Photochem. Conv. Stor. Solar Energy, Cambridge, U.K., August 1978.
4. J. S. Connolly, D. S. Gorman and G. R. Seely, Proc. N.Y. Acad. Sci. 206, 649 (1973).
5. Experiments conducted in the laboratories of Professor Henry Linschitz, Brandeis University.
6. J. Fajer, D. C. Borg, A. Forman, R. H. Felton, D. Dolphin and L. Vegh, Proc. Nat. Acad. Sci. USA 71, 994 (1974).
7. J. Fajer, D. C. Borg, A. Forman, D. Dolphin and R. H. Felton, J. Amer. Chem. Soc. 95, 2739 (1973).
8. J. C. Smart and B. L. Pinsky, J. Amer. Chem. Soc., 99, 956 (1977); J. C. Smart and C. J. Curtis, J. Inorg. Chem. 16, 1788 (1977).
9. B. L. Pinsky, Ph.D Thesis, Univ. Calif., Berkeley (1979).
10. J. C. Smart, B. L. Pinsky, M. F. Frederick and V. W. Day, J. Amer. Chem. Soc. 101, 000 (1979).
11. B. V. Koriakin, T. S. Dzhabiev and A. E. Shilov, Dokl. Akad Nauk. S.S.S.R. 223, 620 (1970); J. -M. Lehn and J.-P. Sauvage, Nouv. J. Chim. 1, 449 (1977); A. Moradpour, E. Amouyal, P. Keller, and H. Kagan, Ibid., 2, 447 (1978); K. Kalyanasundaram, J. Kiwi and M. Grätzel, Helv. Chim. Acta 61, 2720 (1978).

12. C. Creutz and N. Sutin, Proc. Nat. Acad. Sci. USA 72, 2858 (1975).

13. A. Harriman and G. Porter, to be published.

14. R. A. Marcus, Ann. Rev. Phys. Chem. 15, 155 (1966).

15. A. J. Frank, M. Grätzel, A. Henglein and E. Janata, Ber. Bunsenges Phys. Chem. 80, 547 (1976); C. Creutz and N. Sutin, J. Amer. Chem. Soc. 99, 241 (1977); C. D. Jonah, M. S. Matheson and D. Meisel, *ibid.*, 100, 1449 (1978).

16. A. J. Frank, J. W. Otvos and M. Calvin, J. Phys. Chem., in press; Abstract, Second Int. Conf. Photochem. Conv. Stor. Solar Energy, Cambridge, U.K., August 1978.

PUBLICATIONS AND PRESENTATIONS
1978-1979

1. Seibert, M., J. S. Connolly and J. R. Bolton. The Efficiency of Solar Energy Conversion in Photosynthesis, 6th Annual Meeting, American Society for Photobiology, Burlington, Vermont, June 1978.

2. Connolly, J. S. and M. Seibert. Photochemistry and Photobiology at SERI. Abstr., 2nd International Conference on the Photochemical Conversion and Storage of Solar Energy. Cambridge, England, August 1978, pp. 1-2.

3. Connolly, J. S., Photophysical and Photochemical Properties of Bacteriochlorophyll. *ibid.*, pp. 4-6. Also presented at CNRS, Saclay, France. August 1978.

4. Connolly, J. S., R. E. Inman, T. A. Milne, T. B. Reed and M. Seibert. Research Directions in the Biology and Chemical Conversion Branch at SERI. Proc. of the 1978 Ann. Meetings - AS/ISES. pp. 53-55. August 1978.

5. Connolly, J. S., Solar Photochemistry. Biennial Meeting of American Section, International Solar Energy Society, Denver, Colorado. August 1978 (in press).

6. Milne, T. A., J. S. Connolly, R. E. Inman, T. B. Reed and M. Seibert. Research Overview of Biological and Chemical Conversion Methods and Identification of Key Research Areas for SERI. SERI/TR-33-067. September 1978.

7. Connolly, J. S. and J. C. Grosskreutz. The Role of SERI. Symposium on Conversion and Storage of Solar Energy, 30th Southeastern Regional Meeting, American Chemical Society. Savannah, Georgia, November 1978.

8. Seibert, M., J. S. Connolly, T. A. Milne and T. B. Reed. Biological and Chemical Conversion of Solar Energy at SERI. AIChE Symposium Series, 181, Vol. 74, p. 42 (1978).

*9. Frank, A. J., J. W. Otvos and M. Calvin. The Quenching of Rhodamine 101 Emission in Methanol and in Colloidal Suspensions of Latex Particles. J. Phys. Chem. (accepted).

*10. Frank, A. J. and R. J. Hanrahan. The Gas Phase Photolysis of Ethyl Bromide at 253.7 nm. J. Phys. Chem. 82, 2194 (1978).

*11. Frank, A. J. and M. Grätzel. Storage of Light Energy via Photoreduction of Nitrate by Organic Donor Systems in Homogenous and Micellar Solutions. Submitted to Zeitschrift für Naturwissenschaften.

*12. Frank, A. J., J. W. Otvos and M. Calvin. On the Excited Singlet State of Rhodamine 101 and the Surface Effects of Latex Particles in the Promotion of Electron Transfer. Proceedings of the 2nd International Conf. on Photochem. Conv. and Storage of Solar Energy. Cambridge, England, August 1978.

*13. Smart, J. C. and J. L. Robbins. A Low Spin Manganocene and Its Novel Anionic Deriviatives. Synthesis and Characterization of Decomethylmanganocene Complexes. J. Amer. Chem. Soc., 100, 3936 (1978).

*14. Smart, J. C. and C. J. Curtis. Bridging Ligands in Organometallic Chemistry. 2. Synthesis and Reactivity of the Green Dimer of Molybdenocene Containing a Bridging Fulvalene Ligand. Inorg. Chem. 17, 3290 (1978).

*15. Smart, J. C. Chemistry of Metallofulvalene Complexes. Presented at Department of Chemistry, University of Denver, Colorado, November 1978.

*16. Smart, J. C. Chemistry of Metallofulvalene Complexes. Presented at Science Center, Rockwell International, Thousand Oaks, California, November 1978.

*17. Smart, J. C. Chemistry of Metallofulvalene Complexes. Presented at JPL, Pasadena, California, December 1978.

*18. Raymond, K. N., D. P. Freyberg, J. L. Robbins and J. C. Smart. The Crystal and Moleuclar Structures of Decamethylmetallocenes: - Static Jahn-Teller Distortion and Other Effects. ACS/CSJ Chemical Congress, Honolulu, Hawaii. April 1979. Abstr. No. INOR 75.

*19. Smart, J. C. & B. L. Pinsky. Coordinatively Unsaturated Metallofulvalene Complexes of Vanadium. ACS/CSJ Chemical Congress, Honolulu, Hawaii. April 1979. Abstr. No. INOR 504.

---

*Work done elsewhere related to SERI program.

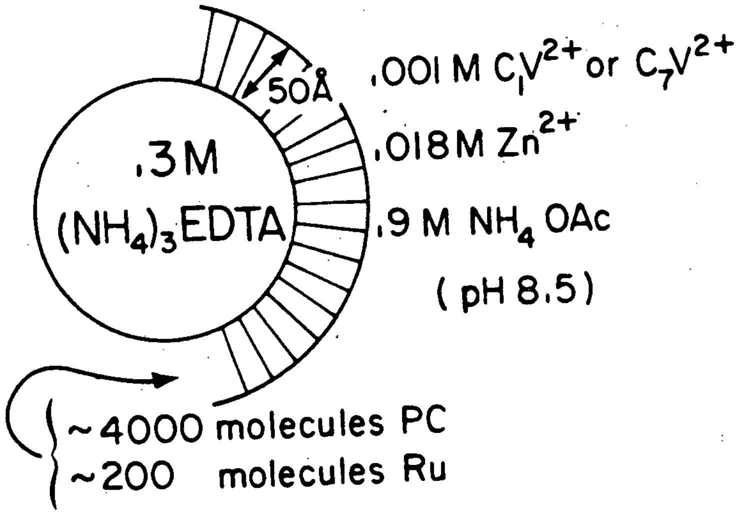
PHOTOSENSITIZED REDOX REACTIONS ACROSS VESICLE MEMBRANES

W. E. Ford*, J. W. Otvos, and Melvin Calvin

Laboratory of Chemical Biodynamics, Lawrence Berkeley
Laboratory, Berkeley, California 94720

We have continued investigation of a model system originally proposed[1] as an example of a dye-photosensitized redox reaction across the walls of phospholipid single-bilayer vesicles (see figure).

Representation of Vesicle Cross-Section



The irreversible oxidation of EDTA (3-) ions, dissolved in the inner aqueous compartments of the vesicle suspension, and one-electron reduction of methyl- or heptylviologen (2+) ions, dissolved in the continuous aqueous phase, is catalyzed by the photoexcited state of a derivative of tris(2,2'-bipyridine)-ruthenium (2+) ion that is incorporated into the vesicle walls. The vesicle walls, which are barriers to ions, prevent complex formation between EDTA and zinc (2+) ions, which inhibits the oxidation of EDTA.[1] The concentration of viologen radical cation formed during intervals of continuous illumination has a sigmoid dependence on the cumulative illumination time. The relative maximum rates of viologen reduction for five cases are tabulated below.

Effect of Vesicle Composition on Relative Maximum Rate

of Viologen Radical Formation[a]

Additional Membrane Components	Viologen (1 mM) in Continuous Aqueous Phase	Color of Incident Light	Relative Maximum Rate
none	C_1V	white[b]	15 ± 3
none	C_7V	blue[c]	105 ± 20
$C_{16}V$(.01 mM)	C_1V	white, blue	100 ± 20
$C_{16}V$(.01 mM) VK (.1 mM) B (.01 mM)	C_1V	white	80 ± 15
$C_{16}V$(.2 mM)	none	blue	1300 ±250

---

[a] Vesicle suspensions contained 2 mM PC and .1 mM Ru; concentrations represent bulk values; pH = 8.5

[b] λ approximately 420 nm to 600 nm.

[c] λ approximately 440 nm to 550 nm, with maximum at 460 nm; incident photon flux was 5-8 x 10^{-7} einsteins sec^{-1} cm^{-2}

When the vesicles are composed of PC, Ru, and $C_{16}V$(mole ratios 200:10:1) and C_1V is dissolved in the continuous aqueous phase (pH 8.5), the maximum quantum yield is .0003 and the reaction rate depends linearly on light intensity. The relative effects of $C_{16}V$, C_7V, and C_1V cations on the reaction rate can be rationalized on the basis of their different degrees of association with the vesicles. Our results suggest that charge transfer across the vesicle walls is electronic in nature since we observe transmembrane redox reactions in the absence of likely diffusional electron carriers.

Abbreviations

EDTA	ethylenediamine-N,N,N',N'-tetraacetate (3-) ion
C_1V	methylviologen = 1,1'-dimethyl-4,4'-bipyridinium (2+) ion
C_7V	heptylviologen
$C_{16}V$	hexadecylviologen
PC	egg yolk phosphatidylcholine
Ru	surfactant tris(2,2'-bipyridine)ruthenium (2+) derivative
NH_4OAc	ammonium acetate
VK	vitamin K_1 quinone
B	decachloro-m-carborane

Reference

1. W. E. Ford, J. W. Otvos, and M. Calvin, Nature 274, 507-508 (1978).

Photoinduced Electron Transfer Across a Water-Oil Boundary: A Model for a Redox Couple Separation

I. Willner,* W. E. Ford, J. W. Otvos, and Melvin Calvin

Laboratory of Chemical Biodynamics, Lawrence Berkeley
Laboratory, Berkeley, California 94720

One approach to the photolysis of water with visible light involves the generation of a redox couple by the use of a mediating sensitizer. However, back reactions of the redox couple represent a basic limitation to the efficiency of these systems. In an attempt to prevent such back reactions, the separation of the redox components in water-oil microemulsions was investigated. The water-in-oil microemulsions were prepared by entrapping water droplets into reversed micelles of dodecylammonium propionate in toluene. The electron transfer process from the aqueous phase into an acceptor located in the interphase region was studied in a system with tris(2,2'-bipyridine)ruthenium(II) ($Ru(bipy)_3^{2+}$) and EDTA in the water phase as photosensitizer and donor, respectively, and hexadecylviologen (HV^{2+}) in the interphase as acceptor. Upon illumination of the system with blue light, the formation of hexadecylviologen radical-cation ($HV^{\dot{+}}$) was observed and monitored by its absorption at 735 nm. The maximum quantum yield obtained was 1.4 ± 0.4%. The results are rationalized by a cyclic redox mechanism mediated by the excited $Ru(bipy)_3^{2+}$ (Figure 1).

The further step of electron transfer across the interphase and into the continuous organic phase is ncessary to achieve a more complete separation of redox components. This process was investigated using two coupled acceptors, viz, 1-benzylnicotinamide (BNA^+), located in the interphase boundary and 4-dimethylaminoazobenzene (Dye) as a solute in the toluene phase. The water droplets again included $Ru(bipy)_3^{2+}$ and EDTA as sensitizer and donor, respectively. Upon illumination, the reduction of the dye into its corresponding hydrazo derivative was observed. Control experiments revealed that all the components included in the system are required for the photoreduction process. A cyclic mechanism is suggested in which the lipophilic, reduced nicotinamide mediates the reduction of the dye in the oil phase (Figure 2). The net reduction of the dye by EDTA is a process that is uphill in free energy ($\Delta G^o \sim 36$ kcal/mole).

The importance of electron transfer processes across water-oil interfaces and their possible utilization in the photolysis of water will be discussed.

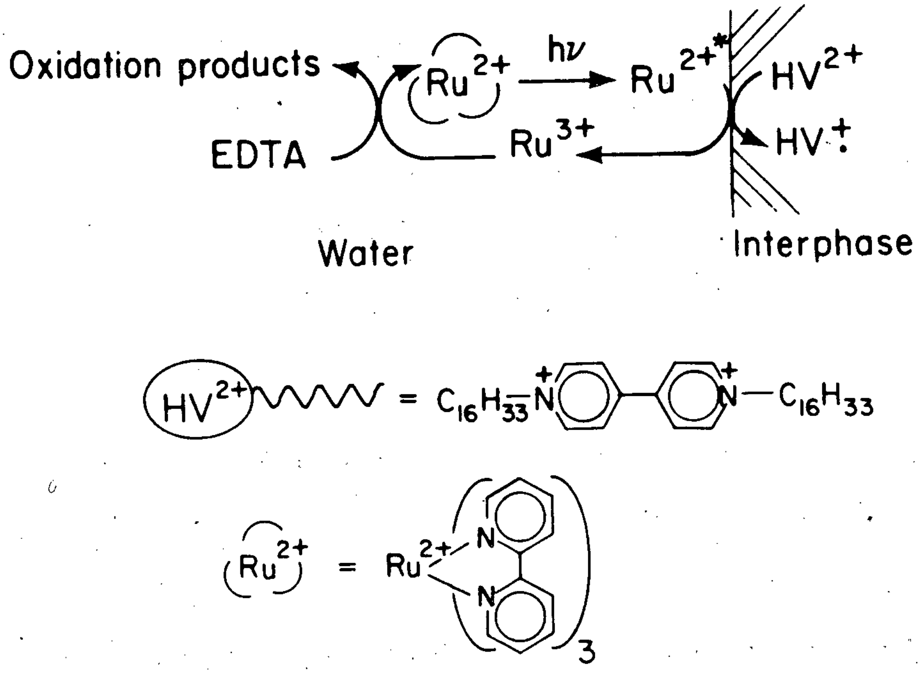


Figure 1. Photoinduced Electron Transfer from Water to Interphase

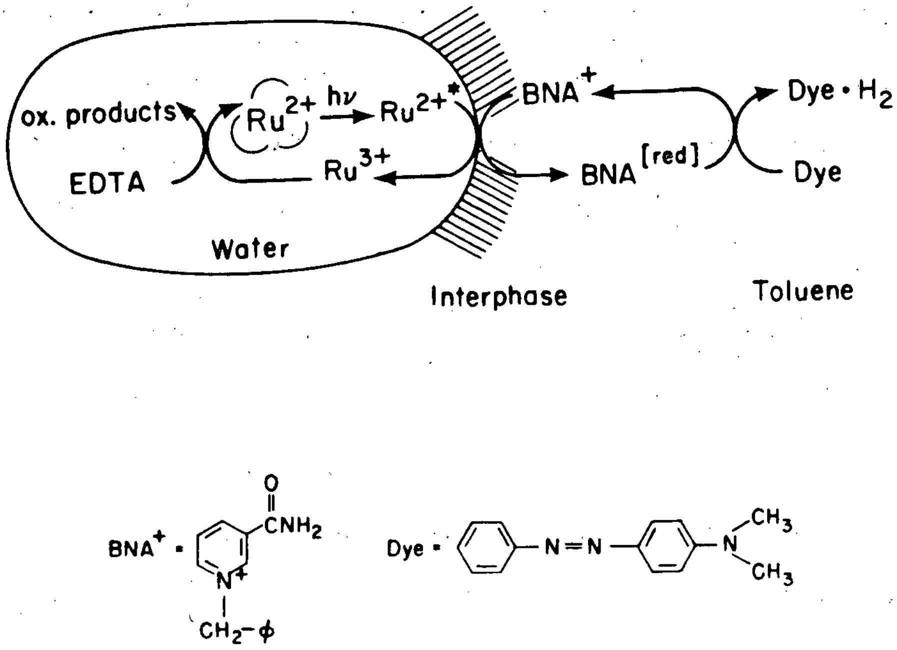


Figure 2. Photoinduced Electron Transfer from Water to Oil Phase

Physical and Chemical Studies
of Chlorophyll in Microemulsions

Raymond A. Mackay
Associate Professor
Department of Chemistry
Drexel University
Philadelphia, PA 19104

The overall objective of this work is to investigate the utility of microemulsions as solvent media for absorbers of solar energy which can act as photosensitizers of redox reactions. These studies will provide fundamental information on the nature of interactions and (photo)reactions at microscopic oil-water interfaces, as well as basis for photochemical energy conversion methods. To this end we have employed the chlorophyll mediated photoreduction of dyes, principally methyl red, by ascorbate in oil in water (o/w) micellar emulsions as our model system.

Previous work (1) has shown that chlorophyll dissolved in an anionic oil/water microemulsion degrades slowly under white light irradiation, but is protected by the presence of a redox system or couple such as azobenzene/hydrazobenzene. Because of its structure, and thus solubility characteristics, the chlorophyll is located in the surface region of the microdroplet.

Initial studies have been designed to provide basic information on sensitized photoreactions in microemulsions. The photoreduction of methyl red and crystal violet has been examined in a sodium cetyl sulfate/pentanol/mineral oil o/w system. Using ascorbate as the water soluble reducing agent and pigment concentrations of less than one per drop ($\leq$ 10 μM), the reaction was found to exhibit a pseudo first order dependence on crystal violet, but a pseudo zero order dependence on methyl red. The effect of sensitizer, ascorbate concentration and light intensity on the quantum yield has also been examined (2). From the results of these and auxiliary studies, a reaction mechanism is proposed which involves the formation of a chlorophyll-dye triplet exciplex rather than any direct intermediacy of an oxidized or reduced pigment species. Based on this scheme, a number of rate constants have been estimated (3).

Some studies have been performed with cationic and nonionic surfactant-stabilized microemulsions. In the non-ionic system, a limiting quantum yield comparable to that in the SCS system has been obtained. A principal difference is that the limiting value is reached at somewhat lower reductant concentrations, consistent with the effect of surface charge on the ascorbate anion. In the cationic system, the limiting value is about threefold less. Present results indicate that the principal effect of surfactant type on the limiting quantum yield is due to surface pH.

A few preliminary studies using other chlorins, principally pheophytin a, have been carried out. The kinetics show evidence of product catalysis, becomming zero order in methyl red only after reaction product has accumulated. The limiting quantum yields are comparable to those obtained with chlorophyll a. In addition, increasing the pH tends to produce zero order kinetics earlier in time but yields a lower limiting quantum yield. For both pigments, oxygen has no net effect on the reaction other than to consume some reducing agent and produce an "induction period". Product accumulation also eliminates the induction period. Work is still in progress, but it appears that the potential reaction product N,N-dimethylphenylenediamine is responsible.

We will continue our investigations of the effect of surface charge, pH and reaction product on the quantum yield of our test system, the chlorophyll sensitized photoreduction of methyl red by ascorbate. We also plan to extend this work to include reversible redox systems, since it is of considerable interest and importance to also control the rate of recombination (back reaction) for practical use as an energy conversion system. The former studies will provide information on the effect of surface charge and polarity on the intrinsic reaction rate. Since metal-free chlorin is an effective sensitizer, we will also examine various synthetic porphyrins. Finally, we plan to conduct laser flash photolysis studies to examine in greater detail the reaction mechanism. For example, our steady-state kinetic results are consistent with the formation of chlorphyll-oxidant triplet exciplex, and it should be possible to obtain direct experimental evidence bearing on this point. Clearly, it is important to elucidate the operative mechanisms since this will permit the extension of the research to other more utilitarian systems.

References

1. C. E. Jones and R. A. Mackay, J. Phys. Chem., 82, 63 (1978).
2. C. E. Jones and R. A. Mackay in "Porphyrin Chemistry; the Symposium held at the MARM of the ACS," F. R. Longo, Ed., Ann Arbor Press (1979).
3. C. E. Jones, C. A. Jones and R. A. Mackay, J. Phys. Chem., , (1979).

LIGHT ENERGY CONVERSION BY BACTERIORHODOPSIN

Lester Packer, Rolf J. Mehlhorn and Alexandre T. Quintanilha

Membrane Bioenergetics Group
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California

This program mainly seeks to characterize the photochemical conversion of solar energy by bacteriorhodopsin, a protein pigment derived from purple membranes of Halobacteria. Unlike photosynthesis, which depends on redox reactions, bacteriorhodopsin operates via a photocycle to develop a proton gradient directly. Bacteriorhodopsin is the simplest and most stable naturally occurring light energy converter presently known. Its photocycle is completed in about 7 msec after light absorption and involves the formation of a number of distinct spectral intermediates which indicate that the environment of the chromophore changes. The essence of the light energy conversion is a vectorial light driven proton translocation coupled to this photocycle.

To find out how protons move in time and space across the membrane which bacteriorhodopsin spans, we have been chemically modifying specific amino acid residues. Thus far we have found that tryptophans appear important for the environment of the chromophore and efficient proton pumping. Another aromatic amino acid has also been implicated as important for activity. One of the eleven tyrosines which are in the molecule has special importance. We will show evidence that this tyrosine is near the surface of the molecule. Five of the six lysines present in the molecule are not important for activity. There is one remaining lysine residue which is believed to be near the retinal chromophore. Future studies will prove the probable importance of this residue as a link in the proton conduction through the molecule and the light energy conversion.

Retinal can be reversibly removed from bacteriorhodopsin. Our studies have identified in bleached bacteriorhodopsin the presence of a proton channel that works, albeit it slowly, in the dark against an electrical energy gradient. We have also carried out studies with tritium and deuterium exchange which reveal that dark adapted and light adapted forms of bacteriorhodopsin have a different conformation or structure. Our studies have shown that the light adapted structure is better able to conduct protons. Based on the studies we have carried out thus far and other work in the literature, we have developed a tentative working hypothesis for the chemical mechanism for the vectorial proton conduction as related to the main phototransients developed in the photocycle.

An important aspect of our program is the use of EPR methods together with spin probes to monitor the electrical properties developed as a result of proton conduction by bacteriorhodopsin. Using a unique charged but also hydrophobic spin probe, we have been able to show that changes in surface charge accompany illumination and are important in the efficiency of the proton conduction. We have been developing a lipid impregnated millipore filter system as an assay for the proton current developed by bacteriorhodopsin and a model of a photovoltaic cell has been constructed. Electrical studies will be an important aspect of our future endeavors.

Future studies will continue to attempt to unravel the mechanism of the light energy conversion in bacteriorhodopsin. A newly discovered light energy converter in a red mutant strain of halobacteria whose membrane pumps protons in an inward direction has been proposed to be a direct mechanism for pumping salt (sodium) will also be studied by similar methods. Future studies will consider the usefulness of such direct methods for salt pumping systems and models of photodesalination.

LIST OF PUBLICATIONS OF PAST TWO YEARS

(EXCLUDING LBL REPORTS)

Konishi, T., Tristram, S. and Packer, L., The Effect of Cross-Linking on Photocycling Activity of Bacteriorhodopsin, Photochem. Photobiol. 29, 353-358 (1979).

Probst, I., Mehlhorn, R., Quintanilha, A. T., Lanyi, J., and Packer, L., Light Induced Transmembrane Proton Fluxes Across Envelope Vesicles of Halobacterium halobium Measured with Spin Probes, Biophys. J. 25, 207a (1979).

Shieh, P. K., Lanyi, J. and Packer, L., Lipid Impregnated Filter Membranes: A Stable Planar Membrane System for Assay of Electrical Properties Across Reconstituted Liposomes and Natural Membrane Vesicles, in: Methods in Enzymology, Volume LV - Biomembranes, Part F: Bioenergetics-Oxidative Phosphorylation (S. Fleischer and L. Packer, eds.), Academic Press, New York, 1979, pp. 604-613.

Mehlhorn, R. J. and Packer, L., Membrane Surface Potential Measurements with Amphiphilic Spin Labels, in: Methods in Enzymology, Volume LVI - Biomembranes, Part G: Bioenergetics: Biogenesis of Mitochondria, Organization, and Transport (S. Fleischer and L. Packer, eds.), Academic Press, New York, 1979, pp. 515-526.

Packer, L., Konishi, T., Scherrer, P., Mehlhorn, R. J., Quintanilha, A. T., Shieh, P. K., Probst, I., Carmeli, C., and Lanyi, J. K., Cation Transport Catalyzed and Coupled to Light Energy Conversion by Bacteriorhodopsin, in: Cation Flux Across Biomembranes (Y. Mukohata and L. Packer, eds.), Academic Press, New York, 1979, pp. 417-429.

Konishi, T., and Packer, L., A Proton Channel in Bacteriorhodopsin, FEBS Lett. 89, 333 (1978).

Quintanilha, A. T., and Mehlhorn, R. J., pH Gradients Across Thylakoid Membranes Measured with a Spin-Labeled Amine, FEBS Lett. 91, 104 (1978).

Konishi, T., and Packer, L., The Role of Tyrosine in the Proton Pump of Bacteriorhodopsin, FEBS Lett. 92, 1 (1978).

Packer, L., Konishi, T., and Criddle, R., Proton Pumps and Channels: Studies with Bacteriorhodopsin and a Proteolipid of the Mitochondrial Adenosine triphosphatase, in: Light Transducing Membranes--Structure, Function, and Evolution, (D. W. Deamer, ed.), Academic Press, New York, 1978, pp. 187-199.

Packer, L., and Konishi, T., Chemical Modification of Bacteriorhodopsin: An Approach to the Mechanism of Proton Translocation, in: Energetics and Structure of Halophilic Microorganisms, (S. R. Caplan and M. Ginsburg, eds.), Elsevier/North-Holland Biomedical Press, Amsterdam, 1978, pp. 143-163.

Konishi, T., and Packer, L., Chemical Modification of Bacteriorhodopsin with N-Bromosuccinimide, FEBS Lett. 79, 369 (1977).

Criddle, R., Packer, L., and Shieh, P., An Oligomycin Dependent Ionophore Protein Subunit of the Mitochondrial Adenosine Triphosphatase, Proc. Natl. Acad. Sci., 74, 4306-4310 (1977).

Konishi, T., and Packer, L., Hydrogen Exchange of Dark-Adapted and Illuminated Bacteriorhodopsin, FEBS Lett. 80, 455 (1977).

Packer, L., Konishi, T., and Shieh, P. K., Conformational Changes in Bacteriorhodopsin Accompanying Ionophore Activity, Fed. Proc. 36, 1819 (1977).

Packer, L., Konishi, T., and Shieh, P., Model Systems Reconstructed from Bacteriorhodopsin, in: Living Systems as Energy Converters, (R. Buvet et al., eds.), Elsevier/North-Holland Biomedical Press, Amsterdam, 1977, pp. 119-128.

Packer, L., Shieh, P. K., Lanyi, J. K., and Criddle, R. S., Use of Lipid Impregnated Millipore Filters for the Direct Measurement of Photopotentials Across Envelope Vesicles of Halobacterium Halobium and for Assay of Ionophore Activity of the Oligomycin Binding Subunit 9 of the Yeast Mitochondrial ATPase, in: Bioenergetics of Membranes, (L. Packer, G. C. Papageorgiou and A. Trebst, eds.), Elsevier/North-Holland Biomedical Press, Amsterdam, 1977, pp. 149-159.

Konishi, T., and Packer, L., Hydrogen Exchange of Dark-Adapted and Illuminated Bacteriorhodopsin, FEBS Lett. 80, 455-458 (1977).

Shieh, P., and Packer, L., Photo-Induced Potentials Across a Polymer Stabilized Planar Membrane, in the Presence of Bacteriorhodopsin, Energy Quarterly, M.O.E.A., 6, No. 4, p. 11 (1977).

Time Resolved Resonance Raman and Fluorescence Studies of the Photosynthetic Proton Pump System of Bacteriorhodopsin

M. A. El-Sayed, James Terner and Joseph Fukumoto
Department of Chemistry
University of California
Los Angeles, California 90024

Bacteriorhodopsin, a retinal-protein complex similar in structure to the visual pigments (1), is the only biological system known to convert light into chemical energy (2), other than the chlorophylls. Bacteriorhodopsin is thought to carry out photosynthesis using a proton pump mechanism by pumping protons across the bacterial cell membrane to produce an electrochemical gradient which drives the synthesis of ATP (3) according to the chemiosmotic theory of Mitchell (4).

The intermediates of the bacteriorhodopsin cycle (Fig. 1) have been extensively characterized by flash photolytic techniques (5). Since the transient absorptions obtained by these techniques are broad, mostly rise and lifetime kinetic data are obtained by these techniques in addition to the position of the visible absorption maxima of the different intermediates. Thus information concerning structural changes (which is necessary for an understanding of the mechanism of the proton pumping process) is usually lacking for the time resolved optical studies. Time resolved vibration spectroscopy (e.g., time resolved Raman spectroscopy) should yield more structural information and can thus contribute to our understanding of the primary processes of the photosynthesis of bacteriorhodopsin.

The intermediates of bacteriorhodopsin are now being investigated by resonance Raman spectroscopy which provides detailed vibrational information about the retinal chromophore. The earliest resonance Raman studies of bacteriorhodopsin concentrated on the bM_{412} and bR_{570} forms which possessed the largest steady state concentrations when a stationary sample was illuminated by continuous wave (c.w.) laser irradiation (6-9). More recently, time-resolved or kinetic resonance Raman spectroscopy in our as well as in other laboratories using pulsed laser (10-14) as well as flow techniques (15-18) has produced complete spectra of bR_{560}^{DA} (13,17,18) and its component isomers (17,18), bL_{550} (18), bM_{412} (11,16,17), bO_{640} (14) and bK_{590} (19). In order to obtain these spectra, we have been developing new laser techniques to determine resonance Raman spectroscopy for short lived intermediates (20). The techniques used vary depending on the lifetime of the intermediate to be studied. All the techniques use lasers as the exciting source, but both c.w. and pulsed lasers are used, depending on whether a flow technique is used or not. In the micro-millisecond time scale, we have developed a technique using a c.w. laser which is amplitude modulated by using rotating choppers (11,12) with one or two slits of variable widths and separated by variable distances. In the microsecond-tens of nanosecond time scale we have used two methods. In one a tightly focused c.w. laser in conjunction with the sample flow technique (19) was used. In the other, a pulsed nanosecond laser was employed (10). In all these methods, an optical multichannel analyzer was used for detection.

In order to determine the retinal Raman spectrum of a specific intermediate, the following procedure was followed: 1) we used the technique appropriate for the rise and decay times of the specific intermediates, 2) a laser wavelength was used to selectively enhance the Raman spectrum of the intermediate studied, and 3) by increasing the laser power one increases the fraction of the photolyzed parent molecule. By using this procedure together with computer subtraction techniques the spectrum of the intermediate under investigation can be extracted.

The time resolved resonance Raman spectra of the retinal in the different intermediates were examined in order to answer the following two questions:
1. Does retinal undergo large conformational changes as the bR molecule goes from one intermediate to the other? 2) When in the cycle is the Schiff base proton ionized?

The first question is answered by following the changes in the 900-1400 cm^{-1}, the so-called fingerprint region of the polyene vibration spectroscopy. The second question can be answered by following the disappearance of the protonated $-C=\overset{+}{N}H$ vibration at ~ 1640-1620 cm^{-1} which is also sensitive to deuteration.

Fig. 2 shows the spectra of the retinal in the different intermediates in the fingerprint region. The proton pump cycle starts with the $bR_{570} \overset{h\nu}{\rightleftarrows} bK_{590} \rightarrow bL_{550} \rightarrow bM_{412}$. During this part of the cycle two protons are believed to be ionized to the medium outside the cell bacteria. From Fig. 2, it is clear that the largest change in the fingerprint region occurs during the first step, i.e., changing $bR_{570} \overset{h\nu}{\rightarrow} bK_{590}$. From the $-C=\overset{+}{N}H$ vibration region, one reaches the conclusion (19) that the bK_{590} is protonated, as is the bL_{550} but not the bM_{412}. This suggests that the Schiff base proton is ionized in the $bL_{550} \rightarrow bM_{412}$ transformation.

The above results indicate that the process of the photon absorption is accompanied by retinal conformational changes (just as in rhodopsin). This seems to trigger protein conformational changes that assist in pumping the two protons to the cell exterior.

Recently, we have focused our attention on the time resolved fluorescence spectroscopy of the protein. In this study (21) two pulsed lasers are used, one to initiate the cycle and the second, delayed by variable amounts of time, to excite the protein fluorescence. The results indicate that no fluorescence intensity changes take place during the first step in the cycle, but in $bK_{590} \rightarrow bL_{550} \rightarrow bM_{412}$ steps the fluorescence intensity decreases to a maximum value at the bM_{412} intermediate. Combining these results with those carried out on the observed changes in the protein absorption (22) (which was explained (22) by a change in 60% of the tyrosine and tryptophan from hydrophobic to hydrophilic medium), one is forced to propose that an effective fluorescence quenching mechanism must accompany the change in the protein environment, e.g., ionization of a proton from tyrosine, protonation of tryptophan or energy transfer from tryptophan to the retinal. The first two are appealing in that they might be involved in the proton translocation process.

References

1. Oesterhelt, D. & Stoeckenius, W. (1971) *Nature New Biol*. **233**, 149-152.
2. Oesterhelt, D. & Stoeckenius, W. (1973) *Proc. Natl. Acad. Sci. USA* **70**, 2853-2857.
3. Racker, E. & Stoeckenius, W. (1974) *J. Biol. Chem*. **249**, 662-663.
4. Mitchell, P. (1966) *Biol. Rev.* (Cambridge) **41**, 445-502.
5. Stoeckenius, W., Lozier, R. H. & Bogomolni, R. A. (1979) *Biochim. Biophys. Acta*, in press.
6. Lewis, A., Spoonhower, J., Bogomolni, R. A., Lozier, R. H. & Stoeckenius, A. (1974) *Proc. Natl. Acad. Sci. USA* **71**, 4462-4466.
7. Mendelsohn, R. (1973) *Nature* **243**, 22-24.
8. Mendelsohn, R., Verma, A. L., Bernstein, H. J. & Kates, M. (1974) *Can. J. Biochem*. **52**, 774-781.
9. Mendelsohn, R. (1976) *Biochem. Biophys. Acta* **427**, 295-301.
10. Campion, A., Terner, J. & El-Sayed, M. A. (1977) *Nature* **265**, 659-661.
11. Terner, J. Campion, A. & El-Sayed, M. A. (1977) *Proc. Natl. Acad. Sci. USA* **74**, 5212-5216.
12. Campion, A., El-Sayed, M. A. & Terner, J. (1977) *Biophys. J*. **20**, 369-375.
13. Terner, J. & El-Sayed, M. A. (1978) *Biophys. J*. **24**, 262-264.
14. Terner, J., Hsieh, C.-L, Burns, A. R. & El-Sayed, M. A. (1979) *Biochemistry*, submitted.
15. Marcus, M. A. & Lewis, A. (1977) *Science* **195**, 1328-1330.
16. Aton, B., Doukas, A. G., Callender, R. H., Becher, B. & Ebrey, T. G. (1977) *Biochemistry* **16**, 2995-2999.
17. Marcus, M. A. & Lewis, A. (1978) *Biochemistry* **17**, 4722-4735.
18. Terner, J., Hsieh, C.-L & El-Sayed, M. A. (1979) *Biophys. J.*, in press.
19. Terner, J., Hsieh, C.-L, Burns, A. R. and El-Sayed, M. A., *Proc. Natl. Acad. Sci. USA*, in press.
20. For a summary see: M. A. El-Sayed, American Chemical Society Symposium Series, "Multichannel Image Detectors in Chemistry," ed. Dr. Y. Talmi, Miami Beach, 1978.

21. El-Sayed, M. A., Fukumoto, J. & Hopewell, W., Biophys. J., in press.

22. Becher, B., Tokunaga, F. & Ebrey, T. (1978) Biochemistry 17, 2293.

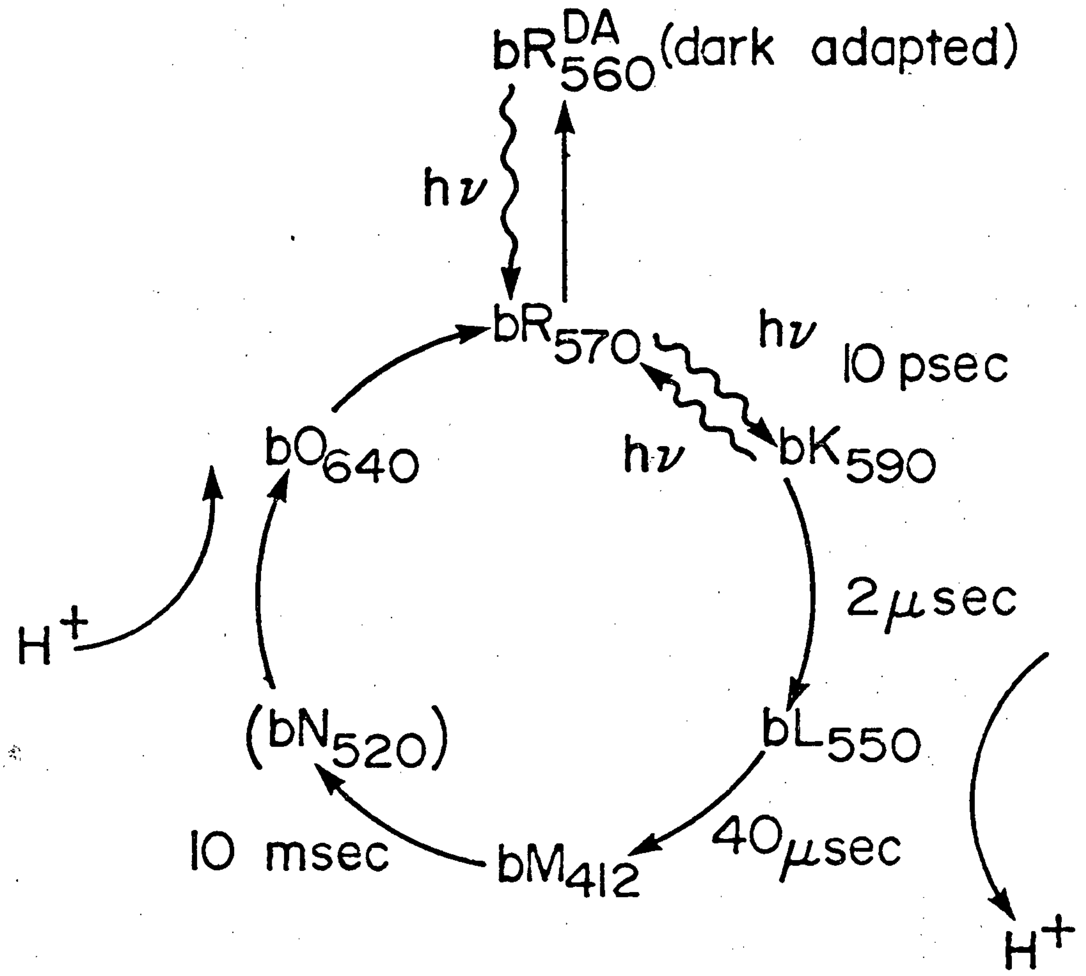


Fig. 1 The photoinitiated proton pump cycle in bacteriorhodopsin.

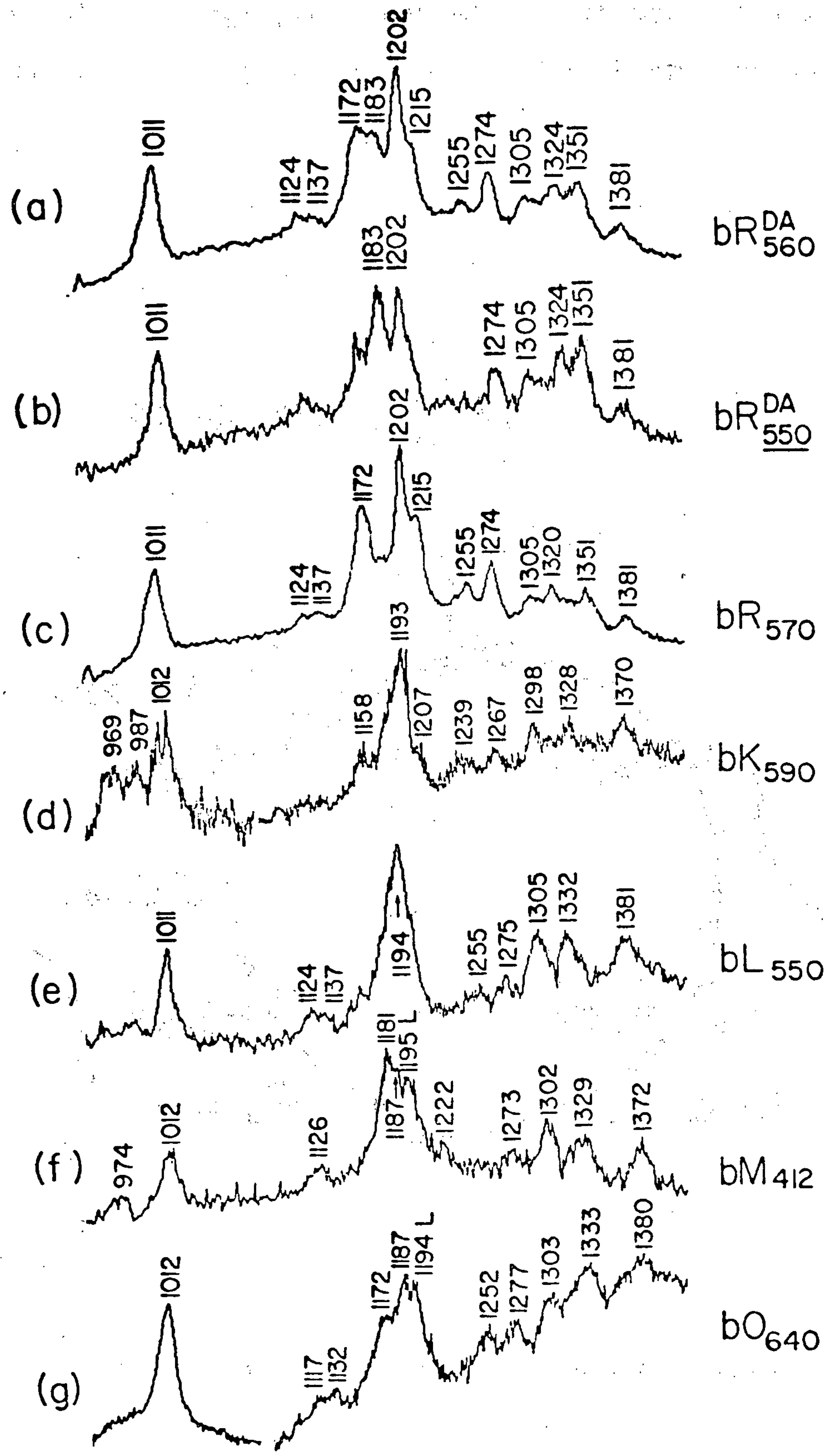


Fig. 2 The Raman spectra in the fingerprint region of the retinal in the different intermediates in bacteriorhodopsin.

CONCENTRATION QUENCHING OF CHLOROPHYLL FLUORESCENCE AND THE QUESTION OF GREEN PLANT ANTENNA

J. C. Hindman, M. J. Yuen, and J. J. Katz

Chemistry Division

Argonne National Laboratory, Argonne, IL 60439

In vivo green plant fluorescence at room temperature is characterized by emission at 685 nm with a low fluorescence quantum yield and a short fluorescence lifetime. As the temperature of a spinach chloroplast is decreased to 100 K there is an increased fluorescence at 735 nanometers and it becomes possible to measure the rates of fluorescence decay for the two different emissions. It has been suggested that the 685 nm emission arises from photosystem II (antenna and whatever chlorophyll forms the active center for this photosystem) and the 735 emission comes from the P700 special pair of photosystem I.

The low fluorescence quantum yield and the short fluorescence lifetime (0.6 μsec) in vivo has been attributed to concentration quenching by the high concentration of chlorophyll (∿0.2 M) in the chloroplast. To determine whether or not this is a reasonable possibility we have undertaken a systematic study of concentration effects on fluorescence lifetimes for in vitro solutions of chlorophyll a, pheophytin a, pyropheophytin a and their covalently linked dimers. For pheophytin a and chlorophyll a the empirical rate equations suggest quenching via energy transfer to weakly or non-fluorescent dimers. For the covalently linked dimers and pyropheophytin a, the data suggest quenching may result from a collisional interaction between the excited S_1 states and ground state molecules. The linked dimers are efficient quenching species. Calculation of a fluorescence lifetime for a hypothetical 0.1 M chlorophyll a solution by extrapolation of our data for either chlorophyll a or the covalently linked dimers yields values close to that observed in vivo. These results support the idea that the short in vivo lifetime could result from interactions between chlorophyll molecules that lead to the formation of quenching species.

Spectroscopic observations on solutions of chlorophylls in methylcyclohexane or toluene containing ethanol as a nucleophile have shown that cooling results in the formation of chlorophyll species with optical properties resembling those of the special pair of photosystem I. The possibility that in vivo reactions centers may also be "self-assembled" is suggested by the increased fluorescence yield at the dimer emission wavelength in chloroplasts cooled to low temperatures. The experimental conditions required for the formation of these "self-assembled" P700 species have been defined, and it has been observed that the optical properties of these "self-assembled" species are similar to those reported for reaction center special pairs and for the folded forms of the covalently linked chlorophyll dimer. The optical data suggest that more than a single species may be formed. Efficient energy transfer from chlorophyll monomer to the P700 species in these systems occurs.

In a continuation of our work on the photophysics of excited chlorophyll states we have measured the absorption spectra of the excited singlet, S_1, and the triplet, T_0, states. The singlet spectrum we measured was found to have features that may be highly significant for energy transfer in photosynthesis. The chlorophyll singlet shows little or no absorption in the wavelength region where S_1 emission (fluorescence) occurs. The lack of significant overlap between the emission and absorption spectrum of the excited state will significantly reduce the probability for resonance energy transfer between two excited singlet molecules and thus decrease the probability for exciton annihilation processes that have been cited as responsible for fluorescence quenching and lifetime shortening in vivo at high photon densities. In related experiments we have found that non-linear absorption and fluorescence quenching in solutions of chlorophyll a irradiated in the region of fluorescence emission can be accounted for by excited state, primarily triplet, absorption.

Chlorophyll b is present in all higher green plants and green algae, but very little is known about its optical properties or the nature of its interactions with chlorophyll a. We have therefore undertaken an examination of the optical properties of chlorophyll b, Chl a/Chl b mixtures, and hydrated Chl a/Chl b systems. A strongly cooled solution of Chl b in ethanol is red-shifted to 662 nm, suggesting the possibility of cross-linked Chl b species that absorb at the λ_{max} of Chl a. Hydrated Chl b absorbs maximally at

685 nm and fluoresces at 690 nm at -85°C. An anhydrous Chl a/Chl b mixture absorbs at 672 nm and fluoresces weakly at 695 nm. These absorbances and emissions are often associated with photosystem II activity and further study of Chl a/Chl b systems is clearly required.

Publications

CHLOROPHYLL LASERS: STIMULATED LIGHT EMISSION BY CHLOROPHYLLS AND Mg-FREE CHLOROPHYLL DERIVATIVES
J. C. Hindman, R. Kugel, A. Svirmickas and J. J. Katz
Proc. Natl. Acad. Sci. USA 74, 5-9 (1977)

LASER PROPERTIES OF SOME PHTHALOCYANINES
R. Kugel, A. Svirmickas, J. J. Katz and J. C. Hindman
Optics. Commun. 23, 189-193 (1977)

STIMULATED FLUORESCENCE AND FLUORESCENCE QUENCHING IN CHLOROPHYLL a AND BACTERIOCHLOROPHYLL a
J. C. Hindman, R. Kugel, A. Svirmickas and J. J. Katz
Chem. Phys. Lett. 53, 197-199 (1978)

COHERENT STIMULATED LIGHT EMISSION (LASING) IN COVALENTLY LINKED CHLOROPHYLL DIMERS
J. C. Hindman, R.Kugel, M. R. Wasielewski and J. J. Katz
Proc. Natl. Acad. Sci. USA 75, 2076-1079 (1978)

DETERMINATION OF THE TRIPLET AND SINGLET ABSORPTION SPECTRA OF CHLOROPHYLL a WITH A TUNABLE DYE LASER
J. Baugher, J. C. Hindman and J. J. Katz
Chem. Phys. Lett, in press.

PERIPHERAL METAL COMPLEXES: CHLOROPHYLL "ISOMERS" WITH MAGNESIUM BOUND TO THE RING E β-KETO ESTER SYSTEM
H. Scheer and J. J. Katz
J. Am. Chem. Soc. 100(2), 561-571 (1978)

CHLOROPHYLL FUNCTION IN THE PHOTOSYNTHETIC REACTION CENTER
J. J. Katz, J. R. Norris, L. L. Shipman, M. C. Thurnauer, and M. R. Wasielewski
Ann. Rev. Biophys. Bioeng. 7, 393-434 (1978)

STUDIES OF CHLOROPHYLL-CHLOROPHYLL AND CHLOROPHYLL-LIGAND INTERACTIONS BY VISIBLE ABSORPTION AND INFRARED SPECTROSCOPY AT LOW TEMPERATURES
T. M. Cotton, P. A. Loach, J. J. Katz, and K. Ballschmiter
Photochem. Photobiol. 27, 735-749 (1978)

A BIOMIMETIC APPROACH TO SOLAR ENERGY CONVERSION
J. J. Katz, T. R. Janson and M. R. Wasielewski
Energy and the Chemical Sciences, S. D. Christian and
J. J. Zuckerman, Eds., Pergamon Press, pp. 31-57 (1978)

STRUCTURE AND FUNCTION OF PHOTOREACTION-CENTRE CHLOROPHYLL
J. J. Katz, L. L. Shipman and J. R. Norris
Chlorophyll Organization and Energy Transfer in Photosynthesis,
CIBA Foundation Symposium 61, 1-40 (1979)

BIOMIMETIC APPROACH TO SOLAR ENERGY CONVERSION: ARTIFICIAL PHOTOSYNTHESIS
J. J. Katz
Proceedings of the 5th Energy Technology Conference,
February 26-March 1, 1978, Washington D. C.,
R. F. Hill, Ed., pp. 499-510 (1978)

BIOMIMETIC APPROACHES TO ARTIFICIAL PHOTOSYNTHESIS
J. J. Katz and M. R. Wasielewski
Biotech. Bioeng. IN PRESS

CHARGE SEPARATION IN SYNTHETIC PHOTO-REACTION CENTERS
J. J. Katz
Proceedings, Dahlem Workshop on Light-Induced Charge
Separation at Interfaces in Biological and Chemical
Systems, Berlin, Germany, October 2-6, 1978, IN PRESS

DETERMINATION OF INTERSUBUNIT DISTANCES AND SUBUNIT SHAPE PARAMETERS IN DNA DEPENDENT RNA POLYMERASE BY NEUTRON SMALL ANGLE SCATTERING
P. Stockel, R. May, I. Strell, Z. Cejka, W. Hoppe,
H. Heumann, W. Zillig, H. L. Crespi, J. J. Katz, and K. Ibel
J. Appl. Crystallography

CHLOROPHYLL-LIPID INTERACTIONS
J. J. Katz
Biochemistry and Physiology of Plant Lipids, L. A. Appelqvist
and C. Liljenberg, Eds., Elsevier/North Holland Biomedical
Press, 1978 IN PRESS

MECHANISMS OF PHOTOCHEMICAL ENERGY CONVERSION BY CHLOROPHYLL

Gordon Tollin, Francesco Castelli, Glen Cheddar & John Hurley
Department of Biochemistry,
University of Arizona,
Tucson, Arizona 85721

Previous work in this laboratory has elucidated various aspects of the mechanism of chlorophyll-photosensitized one-electron transfer reactions in fluid solutions. Our present goals are to explore strategies for increasing the yields of the ion-radical products of such reactions, and for decreasing the probability of product recombination, thereby enhancing the likelihood of secondary electron transfer to species which can be made to do useful work. The systems we are presently studying include chlorophyll dissolved in lipid bilayer membranes (liposomes) and in polymer films. As electron donors and acceptors, we are using quinones, hydroquinones, viologens and iron compounds. Electron spin resonance and laser photolysis techniques are being employed in the investigation of these reactions. The major focus of this work is to increase our understanding of the fundamental mechanisms of chlorophyll one-electron photochemistry and to develop systems which may prove useful for practical solar energy conversion.

Our most recent work in this area has involved the study of the yields and decay kinetics of the chlorophyll triplet state and the chlorophyll cation radical (produced by electron transfer from the triplet state to quinones) in phosphatidyl choline vesicles and in cellulose acetate films. When chlorophyll is dissolved at low concentrations in either of these media, a chlorophyll triplet state transient is easily detectable by laser flash photolysis. The triplet state decays by strictly first order kinetics and has a lifetime which is appreciably longer than in solution (850 μs in the vesicles and 1500 μs in the films vs. 250 μs in degassed ethanol). When the chlorophyll concentration is increased, the triplet lifetime in the vesicles becomes shorter and the decay deviates from first order kinetics. The triplet yield is also diminished at higher chlorophyll concentrations. On the other hand, the chlorophyll triplet lifetime and decay knetics in the films is invariant with chlorophyll concentration, although the yield does decrease at higher concentrations. A comparison of these results with the chlorophyll fluorescence yields suggests the following. In the semi-fluid environment of the lipid vesicles, diffusion of chlorophyll molecules can occur duing the triplet lifetime resulting in quenching by triplet-ground state interaction. In the more rigid film, such diffusion cannot occur and hence quenching is not possible at the triplet level. In both cases, quenching at the singlet level, probably via energy transfer to trapping centers, can take place and thus the triplet yield decreases at high chlorophyll concentrations.

In the vesicles, triplet quenching becomes observable as soon as one introduces more than one chlorophyll molecule into the vesicle. Beyond about 10 chlorophylls per vesicle, the lifetime becomes independent of chlorophyll concentration, even though the triplet yield continues to diminish. This is a consequence of the fact that singlet quenching occurs as soon as the chlorophyll molecules are within a certain critical distance of each other. This, of course, precludes triplet formation and thus the triplet lifetime must reach a limiting value. As expected, we also observe a return to first order decay under these conditions.

When quinones are present, either dissolved within the lipid vesicle or in the surrounding aqueous medium, chlorophyll cation radical formation is observed. The yield of radical formation from the triplet is appreciably less than it is in solution (5-10 times), but the radical lifetime is considerably longer (the second order rate constant, assuming that the reverse electron transfer reaction occurs within the liposome, is approximately 10^3 times smaller). In the films, radical formation does not occur when quinone is also dissolved within the film (presumably due to the high viscosity), but radicals are produced when quinone is dissolved in an aqueous solution in contact with the film. In this case also, yields are slightly lower than in solution (3-5 times) whereas second order rate constants are 10^3 times smaller.

On the basis of the above results, it would appear that placing chlorophyll in a more viscous medium provides a definite advantage over fluid solutions with respect to possibilities for energy conversion, i.e. radical recombination rates are decreased to a much larger extent than are radical yields. We are presently working on determining the effects of chlorophyll concentration, quinone concentration and structure, and liposome and film composition on the yields and lifetimes of the radical products. We hope this will allow us to determine the optimum conditions for energy conversion.

PUBLICATIONS

1. G. Tollin and F. Rizzuto, Photochem. Photobiol. 27, 487 (1978).
2. G. Tollin, F. Castelli, G. Cheddar and F. Rizzuto, Photochem. Photobiol. 29, 147 (1979).
3. F. Castelli, G. Cheddar, F. Rizzuto and G. Tollin, Photochem. Photobiol. 29, 153 (1979).

ELECTRON SPIN ECHO SPECTROSCOPIC STUDIES OF PHOTO-REACTION CENTERS

M. K. Bowman and J. R. Norris
Chemistry Division
Argonne National Laboratory, Argonne, IL 60439

The structural nature of the photosynthetic reaction centers in which light energy is converted into chemical energy is poorly understood. Even the identity of all reaction center components has not been established completely. These photo-reaction centers at one time or another involve the chemistry of free radicals or other paramagnetic species and thus have been explored, almost exhaustively, by application of conventional electron paramagnetic resonance (EPR). Such studies have been most helpful in identifying the participants of photosynthesis such as the chlorophyll special pair but as yet little precise structural information has been provided by EPR or any other method. Conventional EPR in the frequency domain has been an extremely powerful technique for the study of free radicals since the EPR spectrum provides a wealth of information about static interactions and static properties of radical systems. EPR in the time domain, however, records complementary information on the dynamics of the radical and the time dependent properties of the radical system. Thus in order to provide a new approach to the study of photosynthesis we are making extensive use of electron spin echo (ESE) spectroscopy, an advanced form of time domain EPR. ESE spectroscopy obtains structural information in a fairly straightforward manner from the dynamics of the radicals involved in photosynthesis - data that is difficult if not impossible to obtain otherwise.

We have applied ESE in the investigation of several questions in photosynthesis. One aspect in the photosynthetic process is the identity of the components of the "primary event" electron transport chain and the environment of those components. We have investigated this problem by exploiting the nuclear modulation that appears on most ESE spectra. Nuclei which interact weakly with the radical spin produce a modulation governed in part by the hyperfine. These nuclei, which are in or near a free radical, include the nitrogen and magnesium of the chlorophylls. We have measured ^{14}N, ^{15}N and ^{25}Mg modulation from a number of chlorophyll and pheophytin anions and cations _in vitro_ and can distinguish between them. Since the radicals in photosynthetic organisms also exhibit nuclear modulation, we should be able to conclusively identify a number of species involved in electron transfer. As an example of a previously unknown aspect of bacterial photosynthesis, the nuclear modulation effect indicates that a nitrogen containing ligand is associated with the quinone acceptor in bacterial reaction centers. Possible candidates for the nitrogen containing ligand include bacteriochlorophyll, bacteriopheophytin, or protein.

A second question in photosynthesis is the spatial arrangement in the photosynthetic unit. Very little is known about this subject. We have observed the influence of spin lattice relaxation of the iron acceptor on the relaxation of the special pair donor in bacterial reaction centers. Since the size of the effect depends on distance, we have determined the distance between the two components to be about 20 Å. This technique allows us not only to determine distances between other components of the electron transport chain but also to determine the location of the special pair within the reaction center.

A third aspect in photosynthesis is the structure of the *in vivo* special pair. The anisotropy of the triplet state of both the special pair and the chlorophylls *in vitro* make the triplet attractive for studying this question. The intersystem crossing (ISC) rates from T_1 to S_0 provides some information on the physical as well as electronic structure of the special pair. The ESE technique is a convenient method of measuring the ISC rates with fewer complications and errors than conventional EPR and currently has a time resolution of about 6 nsec. In addition the anisotropic nuclear modulation we have observed on ESE spectra of the special pair triplet provides a further probe of its physical structure.

PUBLICATIONS

^{25}Mg HYPERFINE COUPLING IN THE BACTERIOCHLOROPHYLL RADICAL CATION
M. C. Thurnauer, M. K. Bowman, B. T. Cope and J. R. Norris
J. Am. Chem. Soc. 100, 1965-1966 (1978)

ELECTRON SPIN ECHO ENVELOPE MODULATION OF TRAPPED RADICALS IN DISORDERED SYSTEMS: NITROGEN MODULATION FROM ISOTOPICALLY SUBSTITUTED CHLOROPHYLL a CATIONS
M. K. Bowman, S. A. Dikanov, J. R. Norris, M. C. Thurnauer, J. Warden and Yu. D. Tsvetkov
Chem. Phys. Lett. 55, 570-574 (1978)

SUBMICROSECOND TIME-RESOLVED EPR IN LASER PHOTOLYSIS
A. D. Trifunac, M. C. Thurnauer, and J. R. Norris
Chem. Phys. Lett. 57, 471-473 (1978)

ELECTRON SPIN ECHO SPECTROSCOPY AND PHOTOSYNTHESIS
J. R. Norris, M. C. Thurnauer, M. K. Bowman and A. D. Trifunac
Frontiers of Biological Energetics, Vol. I, P. L. Dutton, J. Leigh, A. Scarpa, Eds., Academic Press, pp. 581-591 (1978)

NANOSECOND TIME RESOLVED EPR SPECTROSCOPY EPR TIME PROFILE VIA ELECTRON SPIN ECHO CIDEP
A. D. Trifunac and J. R. Norris
Chem. Phys. Lett. 59, 140-142 (1978)

THE PHOTOEXCITED TRIPLET STATE AND PHOTOSYNTHESIS
H. Levanon and J. Norris
Chem. Rev. 78, 185-198 (1978)

MAGNETIC RESONANCE SPECTROSCOPY OF THE PRIMARY DONOR OF PHOTOSYNTHESIS
J. R. Norris and M. C. Thurnauer
Proceedings, 3rd International Seminar on Energy Transfer in Condensed Matter, Univerzita Karlova, Praha, pp. 72-82 (1978)

OXIDIZED BACTERIOCHLOROPHYLL AS PHOTOPRODUCT IN THE PHOTOSYNTHETIC BACTERIA
James R. Norris and Joseph J. Katz
The Photosynthetic Bacteria, R. K. Clayton and W. R. Sistrom, Eds., Plenum Press, NY, pp. 397-418 (1978)

CHLOROPHYLL FUNCTION IN THE PHOTOSYNTHETIC REACTION CENTER
J. J. Katz, J. R. Norris, L. L. Shipman, M. C. Thurnauer, and M. R. Wasielewski
Ann. Rev. Biophys. Bioeng. 7, 393-434 (1978)

STRUCTURE AND FUNCTION OF PHOTOREACTION-CENTRE CHLOROPHYLL
J. J. Katz, L. L. Shipman and J.R. Norris
Ciba Symposium No. 61, Elsevier, NY, pp. 1-40 (1979)

CHEMICALLY INDUCED MAGNETIC POLARIZATION STUDIES IN RADIATION AND PHOTOCHEMISTRY
D. J. Nelson, A. D. Trifunac, M. C. Thurnauer and J. R. Norris
Rev. Chem. Intermediates IN PRESS

ENDOR SPECTROSCOPY OF THE CHLOROPHYLLS AND THE PHOTOSYNTHETIC LIGHT CONVERSION APPARATUS
J. R. Norris, H. Scheer, and J. J. Katz
Porphyrins, D. Dolphin, Ed., IN PRESS

PROTON-ELECTRON HYPERFINE COUPLING CONSTANTS OF THE CHLOROPHYLL a CATION RADICAL BY ENDOR SPECTROSCOPY
H. Scheer, J. J. Katz and J. R. Norris
J. Am. Chem. Soc. 99(5), 1372-1381 (1977)

THE ORDERING OF THE ZERO FIELD TRIPLET SPIN SUBLEVELS IN THE CHLOROPHYLLS. A MAGNETOPHOTOSELECTION STUDY
M. C. Thurnauer and J. R. Norris
Chem. Phys. Lett. 47(1), 100-105 (1977)

INTERSYSTEM CROSSING IN MOLECULAR DIMERS
M. K. Bowman and J. R. Norris
Chem. Phys. Lett. 54(1), 45-48 (1978)

ELECTRON SPIN LATTICE RELAXATION IN NON IONIC SOLIDS
M. K. Bowman and L. Kevan
Time Domain Electron Spin Resonance Spectroscopy, L. Kevan and R. N. Schwartz, Eds., Wiley-Interscience, NY, 1979, IN PRESS

TIME RESOLVED ELECTRON SPIN ECHO SPECTROSCOPY APPLIED TO THE STUDY OF PHOTOSYNTHESIS
M. C. Thurnauer, M. K. Bowman and J. R. Norris
FEBS Letts. 1979, IN PRESS

PRIMARY EVENTS IN GREEN PLANT PHOTOSYNTHESIS BY TIME-RESOLVED EPR

Marion C. Thurnauer
Chemistry Division
Argonne National Laboratory, Argonne, IL 60439

One of the important problems in photosynthesis is determining the reactions which initially convert the energy of light to useful chemical energy. An understanding of these reactions is required in order to construct useful artificial solar energy devices. In the last few years there has been rapid progress in working out the primary reactions in bacterial photosynthesis. This is mainly the result of applications of new approaches such as picosecond optical spectroscopy. The recent applications of time resolved magnetic resonance to green plant photosynthesis[1] also show great promise. The magnetic resonance approach offers several advantages over optical techniques even though the achievement of picosecond time resolution is not possible. For example, magnetic resonance studies provide the opportunity to study intact photosynthetic units, and the data yields structural information more readily than optical techniques. In addition, the spin polarization (CIDEP) which is observed in the transient radicals of photosynthesis, provides kinetic and mechanistic information. Yet, there are several problems encountered with conventional time resolved epr methods. In order to avoid these problems we are applying to the study of photosynthesis time resolved electron spin echo (ESE) methods which were recently developed at Argonne National Laboratory.[2]

Time resolved ESE avoids the following problems encountered with conventional EPR: (1) inadequate time resolution (our ESE spectrometer has a time resolution of 20 nsec); (2) laser flash interference; (3) artifacts in chemical kinetics due to magnetic relaxation phenomena; and (4) the complications encountered in the proper theoretical treatment of high frequency field modulation EPR. At the same time new data not attainable by conventional EPR is provided. ESE envelope modulation (ESEEM) has been observed in photo induced transient radicals in algae. ESEEM is a new means to directly identify the observed transient radicals by their characteristic modulation pattern. Also a new phenomenon, an echo phase shift (EPS) effect has been discovered in the course of these investigations. All interpretations of this EPS imply that it is quite relevant to interpreting the CIDEP observed in these systems and ultimately the mechanism of the initial photoact.

Using time resolved ESE, we have observed within 40 nsec of laser excitation spin polarized EPR signals in fully deuterated _Synechoccus lividis_ and wild type _S. lividis_. Because of the unique properties of the spin echo technique combined with its inherently superior time resolution, ESE studies have provided the most direct evidence for the existence of several radicals in the early events of green plant photosynthesis. The lifetime of at least one of the early intermediates is determined by the EPS effect to be ∿300 nsec, well below the time resolution of previous studies. We will use examples primarily from our studies of the blue green alga _S. lividis_ (grown in H_2O and D_2O) to describe the technique.

References

1. R. Blankenship, A. McGuire and K. Sauer, Proc. Natl. Acad. Sci. USA 72, 4943-4947 (1975); G. C. Dismukes, A. McGuire, R. Blankenship and K. Sauer, Biophys. J. 21, 239-256 (1978); R. Friesner, G. C. Dismukes, and K. Sauer, Biophys. J. 25, 277-294 (1979); A. R. McIntosh and J. R. Bolton, Nature 263, 443-445 (1976); A. J. Hoff, P. Gast and J. C. Romijn, FEBS Lett. 73, 185-190 (1977); and O. Adrianowycz, K. W. Kinnally, and J. T. Warden, Biophys. J. 25, 52a (1979).
2. A. D. Trifunac and J. R. Norris, Chem. Phys. Lett. 59, 140-142 (1978).

Publications

^{25}Mg HYPERFINE COUPLING IN THE BACTERIOCHLOROPHYLL RADICAL CATION
M. C. Thurnauer, M. K. Bowman, B. T. Cope and J. R. Norris
J. Am. Chem. Soc. 100, 1965-1966 (1978)

ELECTRON SPIN ECHO ENVELOPE MODULATION OF TRAPPED RADICALS IN DISORDERED SYSTEMS: NITROGEN MODULATION FROM ISOTOPICALLY SUBSTITUTED CHLOROPHYLL a CATIONS
M. K. Bowman, S. A. Dikanov, J. R. Norris, M. C. Thurnauer, J. Warden and Yu. D. Tsvetkov
Chem. Phys. Lett. 57, 471-473 (1978)

SUBMICROSECOND TIME-RESOLVED EPR IN LASER PHOTOLYSIS
A. D. Trifunac, M. C. Thurnauer and J. R. Norris
Chem. PHys. Lett. 57, 471-473 (1978)

ELECTRON SPIN ECHO SPECTROSCOPY AND PHOTOSYNTHESIS
J. R. Norris, M. C. Thurnauer, M. K. Bowman and A. D. Trifunac
Frontiers of Biological Energetics, Vol. I, P. L. Dutton, J. Leigh, A. Scarpa, Eds., Academic Press, pp. 581-591 (1978)

MAGNETIC RESONANCE SPECTROSCOPY OF THE PRIMARY DONOR OF PHOTOSYNTHESIS
J. R. Norris and M. C. Thurnauer
Proceedings, 3rd International Seminar on Energy Transfer in Condensed Matter, Univerzita Karlova, Praha, pp. 72-82 (1978)

CHLOROPHYLL FUNCTION IN THE PHOTOSYNTHETIC REACTION CENTER
J. J. Katz, J. R. Norris, L. L. Shipman, M. C. Thurnauer, and M. R. Wasielewski
Ann. Rev. Biophys. Bioeng. 7, 393-434 (1978)

THE ORDERING OF THE ZERO FIELD TRIPLET SPIN SUBLEVELS IN THE CHLOROPHYLLS. A MAGNETOPHOTOSELECTION STUDY
M. C. Thurnauer and J. R. Norris
Chem. Phys. Lett. 54(1), 100-105 (1977)

CHEMICALLY INDUCED MAGNETIC POLARIZATION STUDIES IN RADIATION AND PHOTOCHEMISTRY
D. J. Nelson, A. D. Trifunac, M. C. Thurnauer and J. R. Norris
Rev. Chem. Intermediates (1978) IN PRESS

EPR STUDY OF THE PHOTOEXCITED TRIPLET STATE IN PHOTOSYNTHETIC BACTERIA
M. C. Thurnauer
Rev. Chem. Intermediates (1979) IN PRESS

TIME RESOLVED ELECTRON SPIN RESONANCE OF TRANSIENT RADICALS IN LIQUIDS
A. D. Trifunac and M. C. Thurnauer
Time Domain Electron Spin Resonance Spectroscopy, L. Kevan and R. N. Schwartz, Eds., Wiley-Interscience, NY, 1979, IN PRESS

SPECTROSCOPIC CHARACTERIZATION OF THE PHEOPHYTIN a DICATION
W. Oettmeier, T. R. Janson, M. C. Thurnauer, L. L. Shipman and J. J. Katz
J. Phys. Chem. 81, 339-342 (1977)

TIME RESOLVED ELECTRON SPIN ECHO SPECTROSCOPY APPLIED TO THE STUDY OF PHOTOSYNTHESIS
M. C. Thurnauer, M. K. Bowman and J. R. Norris
FEBS Letts. 1979, IN PRESS

A REVISED Z-SCHEME FOR PLANT PHOTOSYNTHESIS

M. S. Davis, I. Fujita and J. Fajer
Division of Chemical Sciences
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

1. Primary Acceptors in Photosystems I and II

Photosynthesis in algae and green plants functions via two chlorophyll-mediated systems which cooperatively oxidize water (photosystem II, PS II) and reduce carbon dioxide (PS I). PS I utilizes far-red photons ($\lambda \leq 700$ nm) to yield an oxidized chlorophyll pair, $P700^{+\cdot}$ (midpoint potential, $E_m \sim +0.4$ to 0.5 V vs. NHE) and a strong reductant, a bound ferrodoxin with $E_m \sim -0.54$ to -0.59 V, which is capable of reducing the nicotinamide adenine dinucleotide required to fix CO_2. PS II operates in red light ($\lambda \leq 680$ nm) to generate a second chlorophyll cation ($P680^{+\cdot}$) sufficiently electropositive to oxidize water to oxygen ($E_m \geq 0.8$ V) and a weak reductant ($E_m = 0$ to -0.2 V) believed to be a plastoquinone anion radical.

However, recent redox, optical, and magnetic results indicate that additional electron acceptors mediate the transfer of charge from P680 to plastoquinone and from P700 to the iron-sulfur protein.

Substantial evidence exists that monomeric bacteriopheophytin acts as a primary electron acceptor, on a picosecond time scale, in bacterial photosynthesis. Extrapolation to algae and green plants suggests that Pheo or Chl may fulfill a similar role. Redox data indicate that a light-induced charge separation into oxidized Chls ($P680^{+\cdot}$ or $P700^{+\cdot}$) and reduced Pheo is energetically feasible for a single photon event in PS I and II, whereas reduction of Chl is energetically accessible in PS I but less favorable in PS II, if one assumes minimum oxidation potentials of +0.8 V (vs. NHE) for P680 and 0.4 V for P700 and uses in vitro polarographic $E_{1/2}$ of -0.88 V for Chl and -0.64 V for Pheo (in DMF). In PS I, the reaction

$$\mathrm{P700} + \mathrm{Chl} \xrightarrow[700\ \mathrm{nm}]{\text{light}} \mathrm{P700}^{+\cdot} + \mathrm{Chl}^{-}.$$

would result in an energy change, ΔE, of ∿1.3 V and for

$$\mathrm{P700} + \mathrm{Pheo} \rightarrow \mathrm{P700}^{+\cdot} + \mathrm{Pheo}^{-\cdot}$$

$\Delta E \sim 1$ V. In PS II, for

$$\text{P680} + \text{Chl} \xrightarrow[680\text{ nm}]{} \text{P680}^{+\cdot} + \text{Chl}^{-\cdot}$$

$\Delta E \sim 1.7$ V and for

$$\text{P680} + \text{Pheo} \rightarrow \text{P680}^{+\cdot} + \text{Pheo}^{-\cdot}$$

$\Delta E \sim 1.4$ V. (Photons of 700 and 680 nm represent energies of 1.77 and 1.82 eV.)

Klimov et al.(1) noted that the illumination of a Chl protein of PS II, poised at potentials low enough to reduce the canonical plastoquinone acceptor, yields optical changes attributable to reduction of Pheo. Difference spectra for reduction of Pheo and Chl that we have obtained parallel those observed in vivo but a shift of ~20 nm of the Pheo spectrum yields coincidence with nearly all the peaks of PS II. If, as in bacteria, part of the energy of the incident photon is dissipated to effect the rapid primary charge separation, then Pheo rather than Chl seems the acceptor of choice by transducing the 1.82 eV of the impinging photon into 1.4 V of chemical energy. With an estimated reduction potential of -0.64 V, Pheo$^{-\cdot}$ is easily capable of reducing the next electron acceptor, the plastoquinone, with E_m of 0 to -0.2 V. In PS I, Chl, with an in vitro $E_{1/2}$ of -0.9 V, appears the better choice to reduce the bound ferrodoxins, which are the next components in the electron transport chain, with reported E_m as high as -0.59 V. Dynamic polarization effects have been elicited from PS I and are readily ascribed to a radical-radical recombination mechanism involving P700$^{+\cdot}$ and Chl$^{-\cdot}$. Comparison of the optical, magnetic and redox characteristics of Chl$^{-\cdot}$and Pheo^{-} we have obtained in vitro, with those attributed to the short-lived acceptors of PS I and II leads us to conclude that the first reduced chemical products of green plant photosynthesis are the anions of pheophytin in PS II and chlorophyll in PS I. Such a mechanism represents a significantly more efficient conversion of incident light into chemical energy than previously assumed and yields strong reductants to drive the biochemistry of both photosystems I and II.

(1) V. V. Klimov, A. V. Klevanik, V. A. Shuvalov, and A. A. Krasnovskii, FEBS Lett. <u>82</u>, 183 (1977).

2. The Primary Donor of Photosystem II

Magnesium and zinc tetraphenyl chlorins, synthetic models for chlorophyll, exhibit significant variations in the unpaired spin densities of their cation radicals with concomitant changes in oxidation potentials, as a function of solvent and axial ligand. Similar effects are observed for chlorophyll a and its cation radicals. Oxidation potentials for Chl → $Chl^{+\cdot}$ as high as +0.9 V (vs. NHE) are observed in nonaqueous solvents with linewidths of the ESR signals of monomeric $Chl^{+\cdot}$ ranging between 9.2 and 7.8 G in solution. The changes in electronic configuration and ease of oxidation are attributed to mixing of two nearly degenerate ground states of the radicals predicted by molecular orbital calculations.

Extension of these results to P680, the primary donor of PS II, leads us to the following conclusions:
1) since reductions in the linewidth of $Chl^{+\cdot}$ can be achieved by changes in solvent, the linewidth alone cannot be used as a rigorous indicator of the structural nature of Chl in vivo. Without substantiation by other techniques, such as ENDOR, the ESR results reported for $P680^{+\cdot}$ do not, alone, justify the conclusion that it is a dimer. 2) comparison of the optical difference spectrum ascribed to oxidation of P680 with that obtained for the oxidation of monomeric Chl in CH_2Cl_2:THF shows reasonable agreement if the shift from 670 to 680 nm in P680 is attributed to a different coordination of the Chl of P680, possibly involving nearby protein residues. 3) the oxidation potentials found in vitro for monomeric Chl (as high as 0.9 V) approach the limits required for the function of P680 in oxygen evolution. The optical, magnetic and redox properties of ligated, monomeric Chl are thus not inconsistent with those attributed to P680. We suggest, therefore, that P680 is a monomeric chlorophyll whose physical and chemical characteristics, and function as the phototrap of photosystem II are determined by its immediate (protein?) environment. We have incorporated this idea and the postulates regarding the primary acceptors of PS I and II into the revised Z scheme shown in Figure 1 to describe the gross features of electron transport in plant photosynthesis.

Relevant Publications:

Chlorophyll Radicals and Primary Events, J. Fajer, M. S. Davis, D. C. Brune, L. D. Spaulding, D. C. Borg and A. Forman, Brookhaven Symp. Biol. 28, 74 (1977).

Anion Radicals of Bacteriochlorophyll a and Bacteriopheophytin a. Electron Spin Resonance and Electron Nuclear Double Resonance Studies, J. Fajer, A. Forman, M. S. Davis, L. D. Spaulding, D. C. Brune and R. H. Felton, J. Amer. Chem. Soc. 99, 4134 (1977).

Optical and Paramagnetic Identification of a Primary Electron Acceptor in Bacterial Photosynthesis, J. Fajer, M. S. Davis, D. C. Brune, A. Forman and J. P. Thornber, J. Amer. Chem. Soc. 100, 1918 (1978).

Photosynthesis at 1000 nm: Primary Donors and Acceptors, J. Fajer, M. S. Davis, J. P. Thornber and A. Forman, in "Porphyrin Chemistry Advances," F. Longo, Ed., Ann Arbor Science Publishers, Ann Arbor, Michigan, pg. 89 (1978).

Isolated Photochemical Reaction Centers from Bacteriochlorophyll b-Containing Organisms, J. P. Thornber, P. L. Dutton, J. Fajer, A. Forman, D. Holten, J. M. Olson, W. W. Parson, R. C. Prince, D. H. Tiede and W. W. Windsor in "Photosynthesis 77," D. O. Hall, J. Coombs and T. W. Goodwin, Eds., The Biochemical Soc., London, pg. 55 (1978).

Anion Radicals of Pheophytin and Chlorophyll a: Their Role in the Primary Charge Separations of Plant Photosynthesis, I. Fujita, M. S. Davis and J. Fajer, J. Amer. Chem. Soc. 100, 6280 (1978).

Ligated Chlorophylls as Primary Donors in Photosynthetic Oxygen Evolution, M. S. Davis, A. Forman, L. K. Hanson and J. Fajer, Biophys. J. 25, 148a (1979).

Ligated Chlorophyll Cation Radicals: Their Function in Photosynthetic Oxygen Evolution, M. S. Davis, A. Forman and J. Fajer, Proc. Natl. Acad. Sci. (submitted).

Electron Spin Resonance of Porphyrin π Cations and Anions in "The Porphyrins," D. Dolphin, Ed., Academic Press, New York, Vol. IV, pg. 197 (1979).

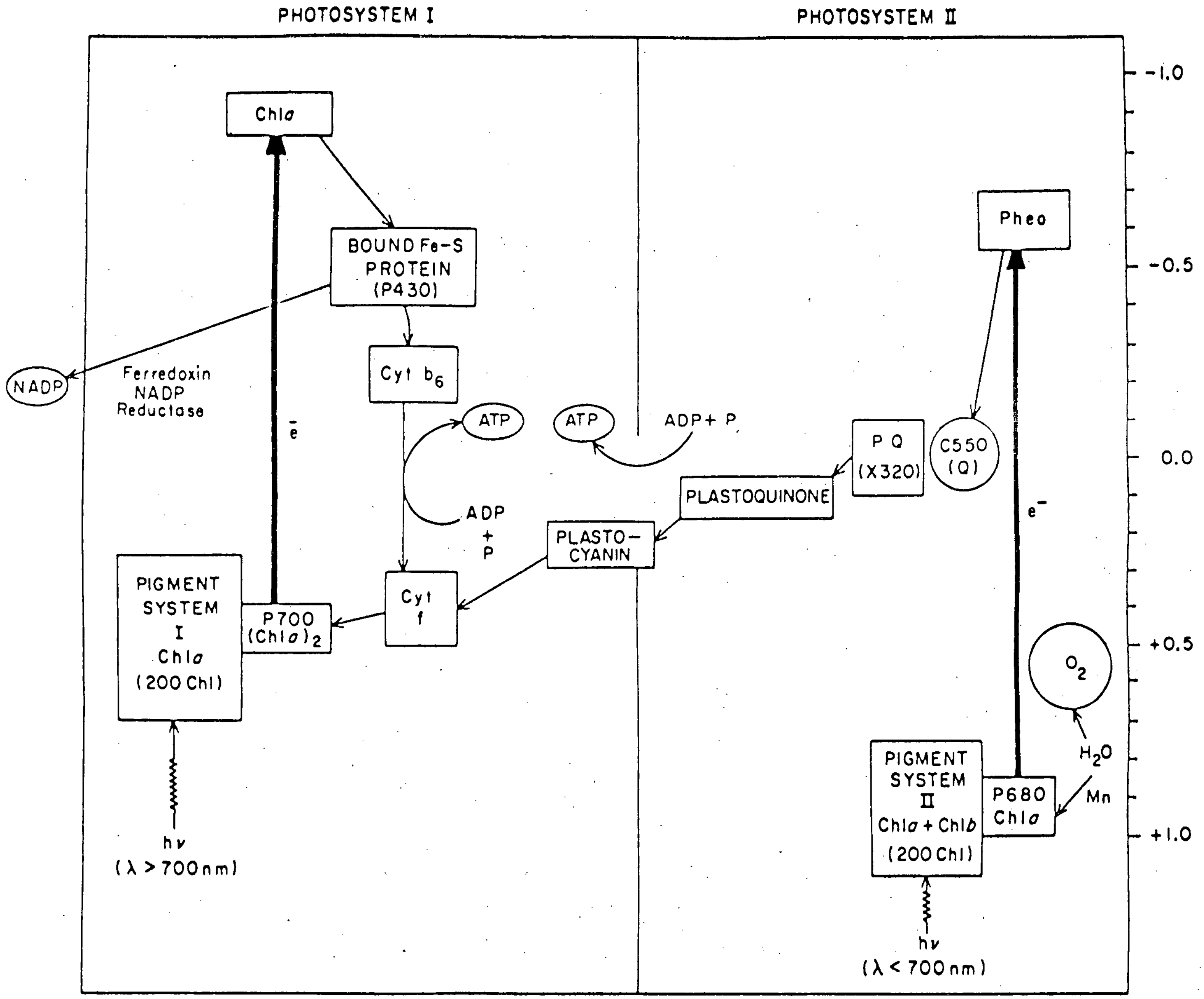


Figure 1: Revised Z-scheme for electron transport of green plant photosynthesis which incorporates monomeric Chl as the primary donor of PS II and pheophytin and Chl as primary acceptors of PS II and I.

Dye-Sensitized Photovoltaic Cells

Terje Skotheim,* John W. Otvos, and Melvin P. Klein

Laboratory of Chemical Biodynamics, Lawrence Berkeley
Laboratory, Berkeley, California 94720

The dye-sensitized photovoltaic cell consists of a wide band-gap, n-type semiconductor substrate (TiO_2 CdS), a thin layer of sensitizer (organic dye) and a semitransparent metal film (Au) evaporated under vacuum on top of the dye. The dye film can be sublimed or cast from solution. The metal is chosen to have a high work function and forms a Schottky barrier when in contact with the semiconductor substrate. The energy levels of the dye are such as to allow tunneling of an electron from the photoexcited dye into the conduction band of the semiconductor where the electric field in the depletion layer pulls it away from the surface (Figure 1).

Most of our work has been done using dyes of the phthalocyanine family (metal free, Cu, Mg) for the following reasons: i) The main absorption in the visible lies in the red and the dyes are transparent in the blue. Coupled with a semiconductor that absorbs in the blue (CdS) the total absorption extends across the entire visible spectrum and the absorption in the semiconductor occurs in the junction region with highly efficient charge separation. ii) The high extinction coefficient ($\varepsilon = 2 \times 10^5 cm^{-1}$) makes it possible to use very thin films (a few hundred angstroms), which increases the efficiency of charge injection. This paper is a discussion of our work with Mg-phthalocyanine sandwiched between a TiO_2 single crystal substrate and a semitransparent gold film.

The photovoltaic action spectra indicate that the main charge-separating barrier is located at the dye/semiconductor interface. For very thin films (100 Å), the photocurrent action spectra for monochromatic light incident through the semiconductor and for light incident through the semitransparent gold film both coincide with the absorption spectrum.

In the case of thicker films (1000 Å), when the light is incident through the gold layer, there is a minimum in the action spectrum at wavelengths near the peak of absorption. Light near the peak will, on the average, be absorbed closer to the metal surface where the excitation is quenched. The quantum yields, defined as the number of electrons per photon incident on the dye layer, are strongly field dependent in accordance with the Onsager theory of geminate recombination. By applying a reverse bias the quantum yield increases to approximately 10% with a field of 4 x 10^5 volts/cm.

There is also an increase in the quantum yield as the film thickness decreases (Figure 2). This is mainly due to the increase in the electric field in the dye layer as we decrease the thickness. Our research aimed at improving the yield is two-fold:

1) Doping of dyes. It has been known for some time that doping p-type molecular solids with electron acceptors increases both dark- and photoconductivity. We have done some initial experiments on doping Mg-phthalocyanine films with iodine by exposing the film to iodine vapor before the gold overlayer is deposited. The best results so far have been a five-fold increase in the quantum yield (Figure 3). This indicates that excitons dissociate upon collision with acceptor impurities as well as at the surface. We are presently determining the optimum dopant concentrations.

2) Exciton quenching at the metal surface. Excitons, upon migrating to the metal surface are quenched very effectively via energy transfer to the metal. The introduction of a thin film of a transparent organic electron donor (2,5 di-tert. Butyl hydroquinone) between the dye and the metal increases the quantum yield. The effect is anomalously large (a factor of 10) for solutions cast films which are known to havelarge pinholes. The evaporated electron donor film therefore prevents the metal from shorting out the dye and provides for a charge separating electric field across the dye.

In the case of sublimed dye films the effect is considerably smaller. Work is in progress to determine the materials conditions, and electronic properties of thin films of electron donors and the interaction between the electron donors and the dye film.

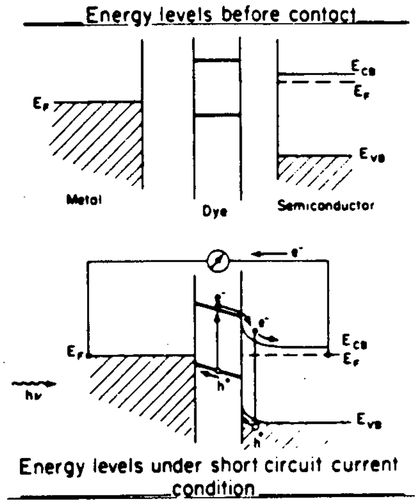


Figure 1. Relative energy levels of metal, dye and semiconductor before and after contact. E_F is the Fermi level, E_{CB} the bottom of the conduction band and E_{VB} the top of the valence band.

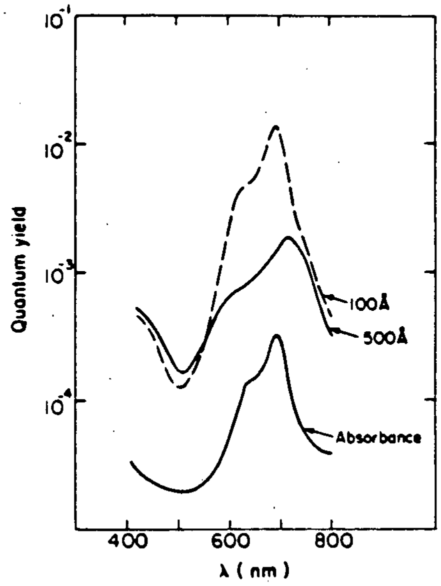


Figure 2. Variation of quantum yield with thickness of dye layer for Au/Mg-phthalocyanine/TiO_2 cells.

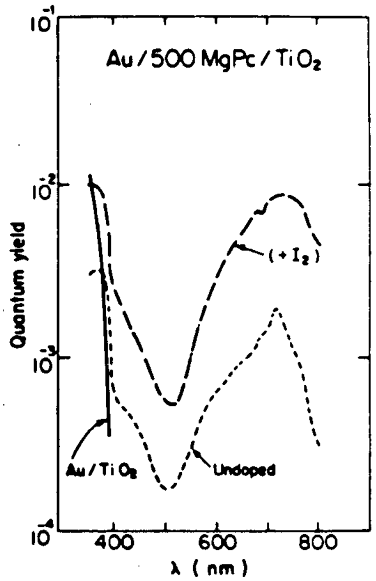


Figure 3. Effect on quantum yield of doping a 500 Angstrom thick film of Mg-phthalocyanine with iodine vapor.

REDOX REACTIONS AT PHOTOELECTRODES PREPARED FROM PHOTOREACTION CENTER MODELS

Michael R. Wasielewski

Chemistry Division

Argonne National Laboratory, Argonne, IL 60439

Over the past two years we have developed a series of dimeric chlorophyll derivatives designed to mimic photoreaction center function in photosynthetic organisms. We are currently studying an extension of these models to include electron acceptors with the aim of producing sustained charge separation. An important facet of this work focuses on the use of these materials as semiconducting electrodes in photoelectrochemical cells designed to catalyze redox reactions for solar energy conversion.

There have been several reports of photoelectrochemical experiments employing chlorophylls a and b, often crude mixtures of the two, to catalyze redox reactions. Large light fluxes are often needed to produce small photocurrents with the result that cell performance degrades as the chlorophyll is photolyzed over time. In our studies we have employed highly stable photoreaction center model compounds that eliminate most of the degradative pathways open to natural chlorophylls, yet retain and at times even improve upon the desirable electronic properties of the parent chlorophylls.

Models thus far examined include magnesium and zinc substituted bis(chlorophyll) cyclophanes, the bis(pyropheophorbide a ethylene glycol monoester) adduct of the pyrochlorophyll a dimer, and several monomeric analogs of these compounds.

In a typical experiment approximately 5-10 nanomoles of model compound is solvent deposited onto a 1 cm^2 polished platinum disc. The resulting photoelectrode is either potentiostated relative to an SCE reference electrode using a 1 cm^2 platinum counter electrode or is connected in series with a load resistor and the counter electrode. In the potentiostated mode photocurrents are measured as a function of redox couple, pH, poised potential, light flux, and wavelength. Open circuit photovoltages are also obtained with a potentiometer. Similar measurements are made with a load resistor and the two electrode configuration to obtain the power output of a given system.

The bis(chlorophyll) cyclophane possessing one magnesium containing macrocycle and one metal-free macrocycle may be used to illustrate the type of data obtained in these experiments. When a photoelectrode prepared from this material is potentiostated at 0 V vs SCE in pH 6.9 phosphate buffer and illuminated with a few milliwatts of light with $\lambda > 450$ nm small ($\sim$0.1 μA) transient cathodic photocurrents are produced. These result from some as yet unknown process but are reminiscent of claims made by other workers for the reduction of water. However, the addition of $\sim$1 mM reducing agent such as hydroquinone to the buffered medium produces an anodic photocurrent of $\sim$10 μA. It is likely that the hydroquinone is being photocatalytically oxidized at the photoelectrode. Benzoquinone in equal concentrations does not yield a similar photocurrent. An action spectrum of these effects shows that the photoreaction center model is the active photocatalyst. Interestingly, the pigment layer is behaving as an n-type semiconductor whereas the great majority of other observations of chlorophyll photoelectrode behavior have noted p-type semiconductor activity.

In an experiment utilizing a 100 Ω load resistor the photocurrent produced by the two electrode cell decreases over a period of several minutes. If on the other hand an equimolar amount of benzoquinone is added to the solution a constant photocurrent density of 8 $\mu A/cm^2$ at a 30 mV photovoltage may be sustained for at least 2 hours. We expect the quantum efficiency of this photoconversion process to be relatively high because only a small fraction of the light is absorbed by the model compound film. We are presently determining this efficiency. The oxidation and reduction of a redox couple at two different electrodes in the same solution with no net loss in oxidized or reduced species yields a liquid junction solar cell which can be used to drive current through an external load.

Several other redox systems have been examined including polysulfide anion, ferri-ferrocyanide, and several ferrocene derivatives. For example, the photoelectrodes respond very well in the polysulfide anion medium yielding current densities of about 10 $\mu A/cm^2$ at photovoltages of 50-75 mV. This power output is sustained for several hours with no apparent degradation of the model compound. These results suggest that photoreaction center models may be successfully employed as polycrystalline semiconducting films in liquid junction solar cells.

Publications

A MILD METHOD FOR THE INTRODUCTION OF MAGNESIUM INTO BACTERIOPHEOPHYTIN *a*
M. R. Wasielewski
Tetrahedron Lett. 1373 (1977)

CONTACT CHEMICAL SHIFTS FOR THE CARBON ATOMS OF NICKEL COMPLEXES OF THE 4-ALKYLANILINES. THE FACTORS GOVERNING THE ELECTRON SPIN RESONANCE HYPERFINE CONSTANTS OF CARBON ATOMS
L. M. Stock and M. R. Wasielewski
J. Am. Chem. Soc. 99, 51 (1977)

A SYNTHETIC BIOMIMETIC MODEL OF SPECIAL PAIR BACTERIOCHLOROPHYLL *a*
M. R. Wasielewski, U. H. Smith, B. T. Cope and J. J. Katz
J. Am. Chem. Soc. 99, 4172 (1977)

9-DESOXO-9,10-DEHYDROCHLOROPHYLL *a*. A NEW CHLOROPHYLL WITH AN EFFECTIVE 20-Pi ELECTRON MACROCYCLE
M. R. Wasielewski and J. F. Thompson
Tetrahedron Lett. 1043 (1978)

BIS(CHLOROPHYLL) CYCLOPHANES. NEW MODELS OF SPECIAL PAIR CHLOROPHYLL
M. R. Wasielewski, W. A. Svec and B. T. Cope
J. Am. Chem. Soc. 100, 1961 (1978)

CHLOROPHYLL
M. R. Wasielewski
Science and Technology Yearbook, McGraw-Hill, New York, NY (1978)

CHLOROPHYLL FUNCTION IN THE PHOTOSYNTHETIC REACTION CENTER
J. J. Katz, J. R. Norris, L. L. Shipman, M. C. Thurnauer, and M. R. Wasielewski
Ann. Rev. Biophys. Bioeng. 7, 393-434 (1978)

COHERENT STIMULATED LIGHT EMISSION (LASING) IN COVALENTLY LINKED CHLOROPHYLL DIMERS
J. C. Hindman, R. Kugel, M. R. Wasielewski, and J. J. Katz
Proc. Natl. Acad. Sci. USA 75, 2076 (1978)

THE TRIFLUOROMETHYL GROUP IN CHEMISTRY AND SPECTROSCOPY. CARBON-FLUORINE HYPERCONJUGATION
Leon M. Stock and Michael R. Wasielewski
Progress in Physical Organic Chemistry, Wiley, New York, NY (1978) IN PRESS

EXCITED AND IONIC STATES OF DIMERIC CHLOROPHYLL DERIVATIVES. BIOMIMETIC MODELLING OF THE PRIMARY EVENTS OF PHOTOSYNTHESIS
M. R. Wasielewski
Frontiers of Biological Energetics, Vol. I, P. L. Dutton, J. Leigh, A. Scarpa, Eds., Academic Press, pp. 63-72 (1978)

A BIOMIMETIC APPROACH TO SOLAR ENERGY CONVERSION
J. J. Katz, T. R. Janson and M. R. Wasielewski
Energy and the Chemical Sciences, S. D. Christian and
J. J. Zuckerman, Eds., Pergamon Press, 1978, pp. 31-57

BIOMIMETIC APPROACHES TO ARTIFICIAL PHOTOSYNTHESIS
J. J. Katz and M. R. Wasielewski
Biotech. Bioeng. 1978, IN PRESS

IN VITRO DUPLICATION OF THE PRIMARY LIGHT INDUCED CHARGE SEPARATION IN PURPLE PHOTOSYNTHETIC BACTERIA
M. J. Pellin, K. J. Kaufmann and M. R. Wasielewski
Nature 278, 54-55 (1979)

THE ELECTROCHEMICAL GENERATION OF CHLOROPHYLL EXCITED STATES
M. R. Wasielewski and A. G. Kostka
J. Am. Chem. Soc. (Submitted 1979)

PHOTOELECTROCHEMICAL PROPERTIES OF METALLOPORPHYRINS

F. J. Kampas, K. Yamashita, C. K. Chang, and J. Fajer
Department of Energy and Environment
Brookhaven National Laboratory
Upton, New York 11973

The primary events of photosynthesis consist of the trapping, transfer and transduction of light into chemical energy within a nanosecond time domain. This is accomplished via an antennae system which funnels the gathered light into reaction centers where rapid charge separation results in electrochemical potential generation and a cyclic electron flow from which useful work evolves. In photosynthetic bacteria, photooxidation occurs with a quantum yield of unity and an initial energy conversion of ∿70%. Recent results suggest that green plant photosynthesis is equally efficient. The information obtained from photosynthesis studies on the identity, electronic configuration, sequence of appearance, kinetics and energetics of the species involved in this very efficient use of light provides the guidelines to devise in vitro photosystems modeled on the biological antennae function and electron transport. In addition, the inherent chemical fragility of chlorophyll derivatives in vitro can be avoided by replacing the naturally occurring pigments with synthetic porphyrins whose chemical and physical properties are readily altered by varying their metal and/or organic framework. Among the many attempts at mimicking the photosynthetic apparatus, Wang(1) described a photoelectrochemical cell which exhibited open circuit photovoltages of ∿1 V and short circuit microamp. currents per cm^2 upon illumination with amber light:

$$-\ \mathrm{Al}\ \left|\ \begin{array}{c}\text{70 monolayers of zinc}\\ \text{tetraphenylporphyrin}\end{array}\ \right|\ \begin{array}{c}\mathrm{Fe(CN)_6^{-3}}\\ \mathrm{Fe(CN)_6^{-4}}\end{array}\ \Bigg|\ \mathrm{Pt}\ +$$

Two such cells in series were reported to oxidize water to oxygen.

The Wang cell and a simpler Ag|porphyrin|Al sandwich cell provide relatively easy experimental methods of systematically screening porphyrins (and other organometallics) for desirable photovoltaic effects.

---

(1) J. H. Wang, Proc. Natl. Acad. Sci. U.S.A. 62, 653 (1969).

To avoid the difficulties associated with multiple Langmuir layers, samples were prepared instead by depositing porphyrin films with a photoresist spinner using dichloromethane as the volatile solvent or by direct sublimation of the porphyrins.

The photoelectrochemical properties of thin films of porphyrins were thus investigated in Al|porphyrin|Ag and Al|porphyrin|$Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$|Pt cells. Action spectra indicate that the photoactive region is the porphyrin-aluminum electrode (Fig. 1). The dark current-voltage (I-V) characteristics of the cells resemble those of a metal-insulator-semiconductor diode and are attributed to an Al-Al_2O_3-porphyrin interface in which the porphyrin acts as a p-type semiconductor and forms a Schottky barrier with the aluminum electrode. The I-V responses to changes in film thickness are consistent with an exponential trap distribution in the porphyrin film.

The physical and chemical properties of the porphyrins were systematically altered by varying the metal and organic framework of the porphyrins. The photovoltaic behavior of ms tetraphenyl-, ms tetrapropyl- and octaethyl porphyrins, porphins, chlorins, co-facial diporphyrins and mesoporphyrin esters were investigated. Peak quantum yields (calculated for short-circuit currents obtained on illumination through the semi-transparent aluminum electrode at the major absorption band of the porphyrins) ranged from 10^{-1} to 10^{-4} at wavelengths of 400-450 nm (Fig. 2). Films prepared by rapid evaporation of concentrated porphyrin solutions were ∿50% more effective than films prepared by sublimation. The latter were found to be microcrystalline by electron microscopy at 20,000-fold magnification. For a given ligand, quantum efficiencies of the photocurrents paralleled the first oxidation potential of the porphyrins: the more easily oxidized compounds exhibited the higher quantum yields (Fig. 3). No obvious correlations were discerned between quantum yields and luminescent properties of the porphyrins. Power conversion efficiencies varied from 10^{-2} to 10^{-6} for monochromatic light with magnesium tetraphenyl porphyrin and cadmium porphin yielding open circuit voltages of ∿1 volt and ∿1% power conversions. The effects of film morphology, the use of other metals of low work functions, of semiconductor electrodes and of porphyrin with expanded π systems such as tetrabenzporphyrins, are under investigation.

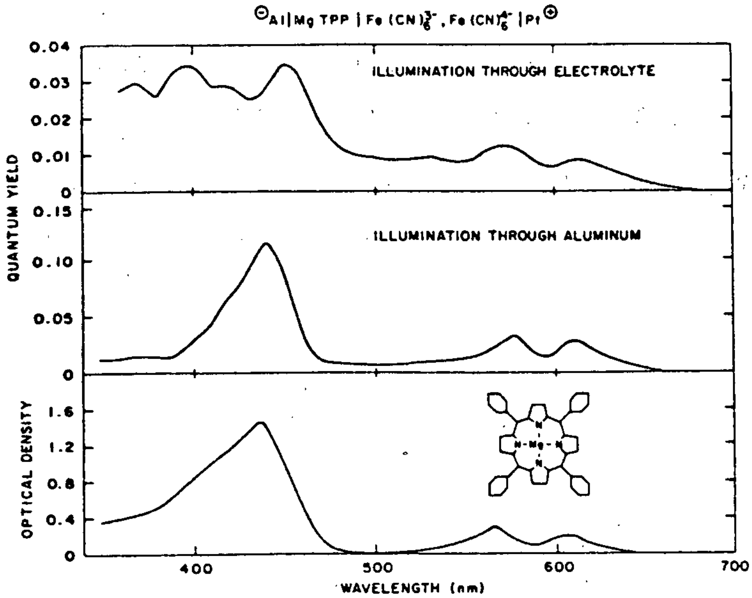


Fig. 1. Comparison of the optical spectrum of a magnesium tetraphenylporphyrin film with the action spectra obtained for the cell shown on illumination of the Al/porphyrin and Pt/electrolyte/porphyrin electrodes. Note the large differences in photocurrent quantum yields at the two interfaces.

Al | Porphyrin | $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ | Pt

Peak Quantum Yields

Compound	Wavelength (nm)	Quantum Yield
CdP	410	.19
MgP	420	.18
ZnP	420	.09
MgTPP	445	.10
CdTPP	450	.041
ZnTPP	440	.0048
PdTPP	440	.0012
H_2TPP	445	.00071
CuTPP	430	.00066
CoTPP	430	.00012
PtTPP	430	.00007
MgTPC	440	.044
ZnTPC	435	.012
ZnTPiBC	425	.055
ZnOEP	400	.024
MgOEP	420	.015
PdOEP	405	.014
PtOEP	390	.0095
H_2OEP	415	.0038
MgOEC	420	.014

P - Porphin; TPP - Tetraphenylporphin
TPC - Tetraphenylchlorin; TPiBC - Tetraphenylisobacteriochlorin
OEP - Octaethylporphin; OEC - Octaethylchlorin

Fig. 2. Photocurrent quantum yields at the wavelength of maximum absorption for the cell shown as a function of porphyrin and metal.

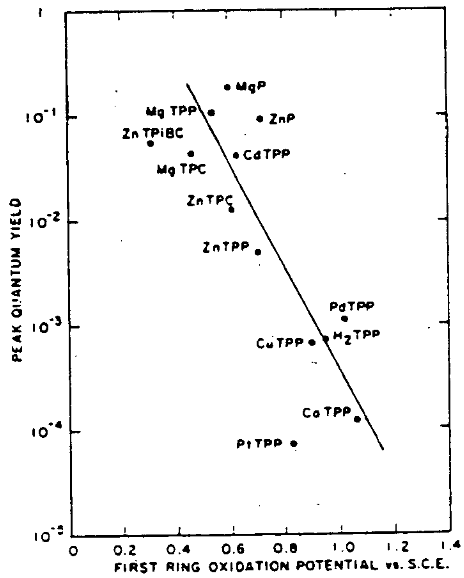


Fig. 3. Correlation between the first oxidation potential of the porphyrins in nonaqueous solvents and peak quantum yields.

Publications:

F. J. Kampas, K. Yamashita, C. K. Chang, and J. Fajer. Photoelectrochemical Properties of Metalloporphyrins. J. Electrochemical Soc. (in press).

F. J. Kampas, K. Yamashita, and J. Fajer. Photovoltaic Properties of Metalloporphyrins (submitted to Nature).

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720