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May 1980

SERI/PIRDES Workshop on Photoconversion of Solar Energy

Needs and Opportunities for Research in Photoconversion of Solar Energy

Keystone, Colorado 24 - 26 October 1979

John S. Connolly and Francis Garnier, Cochairmen

Solar Energy Research Institute
A Division of Midwest Research Institute

1536 Cole Boulevard
Golden, Colorado 80401

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NEEDS AND OPPORTUNITIES FOR RESEARCH IN PHOTOCONVERSION OF SOLAR ENERGY

KEYSTONE, COLORADO
24-26 OCTOBER 1979

JOHN S. CONNOLLY, COCHAIRMAN
FRANCIS GARNIER, COCHAIRMAN
LOIS BLACKWOOD, CONFERENCE COORDINATOR

MAY 1980

PREPARED UNDER TASK NO. 3322.20

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PREFACE

This joint U.S./French Workshop on Photoconversion of Solar Energy was made possible by the foresight and vision of two men: Dr. Paul Rappaport, founding Director of the U.S. Solar Energy Research Institute (SERI) and Dr. Michel Rodot, Director of the French C.N.R.S. Programme Interdisciplinaire pour la Recherche et Developpement de l' Energie Solaire (PIRDES). In October 1978, they signed a memorandum of agreement establishing an informal cooperative arrangement between SERI and PIRDES. The first project was this workshop.

The purpose of this informal meeting was to bring together French and U.S. scientists working in the areas of photobiology, photochemistry, and photoelectrochemistry to exchange information on solar research of common interest. This report summarizes some of the needs and opportunities for solar-related basic research in these three areas of photoconversion. The longer term goal was to lay the foundation for future interactions, such as joint research programs and exchange of visiting scientists, as well as to continue the workshop series on an annual or biennial basis.

SERI hosted this premier event and Drs. John S. Connolly (SERI) and Francis Garnier (PIRDES) were cochairmen. The site was selected to take advantage of the Colorado scenery in proximity to SERI and to provide a setting conducive to exchange of ideas and the establishment of new relationships. Judging from the response of the attendees, the facilities at Keystone, Colorado, about 120 km from Golden, appeared to meet these as well as other criteria. Unfortunately, neither Dr. Rodot nor Dr. Rappaport was able to attend - the former because of a travel conflict, the latter due to ill health.

I am saddened to report that Dr. Paul Rappaport died on April 21, 1980. He was loved and respected by those who knew him, and he will be missed by the entire international community of solar scientists. As a small token of our appreciation for his encouragement and guidance, this brief report of the first SERI/PIRDES Workshop on Photoconversion of Solar Energy is dedicated to his memory.

John S. Connolly

John S. Connolly

Approved for:

SOLAR ENERGY RESEARCH INSTITUTE

K. J. Touryan

K. J. Touryan
Deputy Director

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PRÉCIS OF GROUP DISCUSSIONS

Photobiology

Michael Seibert and Jean Lavorel, Discussion Leaders

Photochemistry

John S. Connolly and Francis Garnier, Discussion Leaders

Photoelectrochemistry

Arthur J. Nozik and Gerard Lepoutre, Discussion Leaders

PHOTOBIOLOGY

I. General Points

A. Can knowledge of structure and function of biological systems help photochemists who are working on synthetic systems?

B. Most biological (photosynthetic) applications are long-term and eventual success requires increased basic research knowledge.

C. Greater use should be made of marine organisms and systems.

D. Continuity of funding, at whatever level, is critical for continued progress in this area. Continuous moderate funding is better than high peaks and low valleys.

E. It would be dangerous to couple support of photosynthesis research to the energy crisis.

II. Problem Areas

A. Primary processes

1. Structure and function of RCs, PSI, and PSII
2. The "special pair" — Is it always necessary?
3. Relationship between antenna pigments and RCs (structure and function)
4. The fluorescence yield of PSI — Why is it so low?
5. Stability of charge separation — Why so many steps?
6. Enhanced absorption at high light intensity

B. O_2 evolution

1. What are the structure and function relationships of the O_2 evolution apparatus?
2. Is biological water-splitting the most efficient mechanism?
3. How does PSII protect itself from strong oxidants produced by the photochemistry?
4. At what stage is water split?
5. Can manganese be replaced by other metals?

C. Mechanism and regulation of electron transport and energy conversion - utilization of photosynthetically generated reductants by different pathways (e.g., hydrogenase, nitrogenase)

D. Stability (protection and repair mechanisms) — How does the biological system (or organism) maintain pigments and proteins in a stable form, particularly in the light?

E. Stress

1. Mechanisms of resistance to stress (e.g., water, salt, heat, CO_2-deprivation, high light intensity, pressure, cold)

2. In particular, what is the mechanism of thermal resistance of the water-splitting system in thermophilic organisms? This information could be particularly useful in understanding any possible relationship between structure and stability.

F. Carbon metabolism

1. Increased efficiency

2. Decrease of photorespiration (or better, control of the process at times when it is unnecessary)

3. Biochemistry and regulation of natural products

III. Opportunities for Interactions between Photochemistry and Photobiology

A. Application of physical theories to biological energy- and electron-transfer processes

B. Biological sensitizers for coating semiconductor electrodes

C. Biological systems as models for photochemical reactions

PHOTOCHEMISTRY

I. Short-Term Problems

A. Compilation of structure-property relationships of organic, inorganic and organometallic systems of interest to photochemical conversion and storage. Properties include geometry and electronic structure, spectroscopy, photophysics, photochemistry and electrochemistry, as well as other chemical and physical properties of the ground states. An evolutionary (computerized) data base is needed to provide the framework for designed synthesis of new compounds suited to specific reactions.

B. Systematic studies of both forward and back reactions in photoredox systems, including variations of solvent, temperature, etc.

C. Fundamental studies of spectroscopic and photophysical parameters of photosensitizers, including natural compounds (e.g., porphyrinic systems), and effects of environment and aggregation

D. Realistic models for calculations of solar efficiencies of photochemical processes. Also, there is a need for a common understanding of terminology among all disciplines working on quantum conversion processes.

E. Studies of electron- and energy-transfer processes at interfaces (e.g., membranes)

F. Synthesis and characterization of new complexes and assemblies for redox catalysis and photosensitization as well as for probes and model systems

II. Long-Term Problems

A. Establishment of criteria for prediction of fates of excited states (e.g., energy vs. electron transfer)

B. Determination of structures of excited states and intermediates, including geometric and electronic parameters

C. Theoretical studies of electron transfer in heterogeneous systems

D. Spectroscopic, photophysical, and photochemical studies of metal clusters, polynuclear complexes, and molecular assemblies containing multiple chromophores

E. Experimental studies of multiphoton, multielectron photoredox reactions leading, for example, to reduction of nitrogen and carbon dioxide

F. Generation and properties of unusual oxidation states

III. Approaches

A. Flash photolysis - subpicosecond to millisecond

B. Pulse radiolysis, T-jump, P-jump, and other relaxation techniques

C. Resonance Raman spectroscopy - CW and time-resolved

D. EXAFS of excited states

E. NMR of excited states and intermediates

F. ODMR

G. ESR, ENDOR, and ESE (Electron Spin Echo) spectroscopy

H. Synthesis of new sensitizers, synthetic membranes, and photocatalytic systems

IV. General

A. Interfaces

1. Photobiology: properties of membranes especially with respect to electron and ion transport; chemical analogs of hydrogenase, nitrogenase, and methanogens; understanding of O_2-evolution in PSII; how have biological systems "solved" the problem of the back reaction(s)?

2. Photoelectrochemistry: electron transfer at membranes; chemically modified electrode surfaces; nonequilibrium processes

B. Long-term considerations — temperature, toxicity, cost, efficiency, quantum yields, effects of O_2 (especially in water-splitting systems), effects of impurities (e.g., in commercial-grade chemicals)

PHOTOELECTROCHEMISTRY

I. Theory and Models

A. Thermodynamic limits on conversion efficiencies

B. One-step vs. two-step processes (photoelectrochemistry alone vs. photovoltaics plus dark electrochemistry)

C. Theory of surface states and their role(s)

D. Theory of electron and hole storage in metal and semiconductor electrodes (details of reaction mechanisms)

E. Theory of nonequilibrium processes (hot electron and hole injection; irreversible redox processes)

F. Theory of semiconductor electrode behavior (correlation of band gap, flatband potential, and stability)

II. Materials and Systems

A. Biological hybrid systems on electrodes

B. Proton-pump systems for energy conversion and storage; light-driven proton pumps for reducing overvoltages

C. New semiconductor electrode materials

1. Nonbonding transitions (e.g., layered compounds)

2. New oxide semiconductors

3. Derivatized (i.e., surface-modified) electrodes

4. Organic and organometallic semiconductors

5. Dye-sensitized electrodes

6. Multilayered electrodes

7. Multiband semiconductors

III. Novel Systems, New Opportunities

A. Dispersed microstructures

B. Novel chemistry

1. N_2 fixation

2. CO_2 reduction

3. Peroxide formation

C. Combinations of semiconductors and membranes to achieve novel conversion schemes (e.g., saltwater desalination)

D. Regenerative electrode systems for homogeneous photochemical reactions

E. New electrolytes

1. Solid electrolytes

2. Nonaqueous electrolytes

3. Room-temperature molten salts

F. Hot carrier photoelectrochemistry

G. In-situ surface analysis

H. In-situ storage (photovoltaic cells)

IV. Opportunities for Interface with other Conversion Technologies

A. Photobiology

1. Help in understanding primary processes for building artificial systems

2. Analogies between PSI and PSII and p- and n-type semiconductors

3. Catalysis on semiconductors vs. catalysis in photochemical and biological systems

B. Photochemistry

1. Catalysis

2. Regeneration of dyes for homogeneous reactions

3. Understanding of electrochemistry of excited electronic states in photochemical reactants

C. Photovoltaics — Problems are common whether generating electricity or fuels.

SERI/PIRDES WORKSHOP ON PHOTOCONVERSION

Keystone, Colorado; 24-26 October 1979

AGENDA

Wednesday, October 24

10:00 a.m.	Welcome to SERI - Building 9, Room 254
10:30 a.m.	Presentation on SERI Permanent Site - G. Cavanaugh
11:00 a.m.	Overview of SERI Programs - Dr. K. Touryan, Acting Director of Technology Development
11:30 a.m.	Tour of Biological and Chemical Conversion Branch
12:00 noon	Luncheon - Building 9, 4th Floor Introductory Remarks - Dr. Paul Rappaport
1:30 p.m.	Tour of SERI Laboratories
3:15 p.m.	Bus departs for Keystone (east parking lot, Building 9)
5:00 p.m.	Check into Keystone Lodge
6:00 p.m.	Cash Bar - Tenderfoot Lounge
7:00 p.m.	Dinner - Foxfire Room
8:30 p.m.	Session I, General - Windwood Room

Thursday, October 25

9:00 a.m.	Session II, Photochemistry - Arapahoe Room
10:20 a.m.	Coffee Break
10:40 a.m.	Session III, Photochemistry
12:00 noon	Lunch (at liberty)
2:00 p.m.	Session IV, Photoelectrochemistry - Arapahoe Room
3:20 p.m.	Coffee Break
3:40 p.m.	Session V, Photoelectrochemistry
6:00 p.m.	Dinner (at liberty)
8:00 p.m.	Session VI, Photovoltaics - Arapahoe Room

AGENDA (continued)

Friday, October 26

9:00 a.m.	Session VII, Photobiology - Arapahoe Room
10:20 a.m.	Coffee Break
10:40 a.m.	Session VIII, Photobiology
12:00 noon	Working Luncheon - Arapahoe Room
2:00 p.m.	Session IX, General Discussion - Arapahoe Room
3:00 p.m.	Open
5:15 p.m.	Bus departs Keystone Lodge for El Rancho
6:30 p.m.	Cocktails
7:30 p.m.	Dinner
9:30 p.m.	Bus departs El Rancho for Holiday Inn, Golden

SERI/PIRDES WORKSHOP ON PHOTOCONVERSION

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PROGRAM

Wednesday, October 24

8:30 p.m.	Session I, General Chairman	Windwood Room J. S. Connolly
8:40 p.m.	PIRDES Perspective of Photoconversion	F. Garnier, J. Lavorel
9:10 p.m.	SERI Perspective of Photoconversion	A. J. Nozik

Thursday, October 25

9:00 a.m.	Session II, Photochemistry Chairman	Arapahoe Room J. C. Smart
	Needs and Opportunities for Solar Photochemistry	J. S. Connolly
	Problems Concerning Photosensitizers	F. Garnier
	Problems in Electron Transfer	N. Sutin
	Discussion	
10:20 a.m.	Coffee Break	
10:40 a.m.	Session III, Photochemistry Chairman	Arapahoe Room A. J. Frank
	Electron Transfer In Homogeneous and Heterogeneous Media	C. Giannotti
	Photoredox Reactions in Organized Assemblies	D. G. Whitten
	Photochemical Hydrogen and Oxygen Production	J.-P. Sauvage
	Photochemical Hydrogen Production	A. Moradpour
12:00 p.m.	Lunch (at liberty)	

PROGRAM (continued)

2:00 p.m.	Session IV, Photoelectrochemistry Chairman	Arapahoe Room G. W. Murphy
	Photosensitized Electrodes and Interfaces	G. Lepoutre
	Photo-induced Charge Transfer through Membranes	C. Gavach
	Discussion	
3:00 p.m.	Coffee Break	
3:20 p.m.	Session V, Photoelectrochemistry Chairman	Arapahoe Room J. A. Turner
	Problems in Photoelectrochemistry	A. J. Nozik
	Novel Chemistry at Semiconductor Electrodes	A. J. Bard
	Theoretical Problems	F. Williams
	Discussion	
6:00 p.m.	Dinner (at liberty)	
8:30 p.m.	Session VI, Photovoltaics Chairman	Arapahoe Room J. S. Connolly
	SERI-Managed Programs in Electrochemical Photovoltaic Cells and Fluorescent Concentrators	S. Deb
9:00 p.m.	General Discussion	
Friday, October 26		
9:00 a.m.	Session VII, Photobiology Chairman	Arapahoe Room P. Weaver
	Photobiological Energy Conversion	M. Seibert
	Structure and Function of Photosynthetic Systems	J. Breton
	Photosystem I Phenomena	A. San Pietro
	Discussion	
10:20 a.m.	Coffee Break	

PROGRAM (continued)

10:40 a.m.	Session VIII, Photobiology Chairman	Arapahoe Room S. Lien
	Photosynthetic Oxygen Production	P. Joliot
	Photosystem II Phenomena	W. Butler
	Fluorescence and Delayed Light Emission	J. Lavorel
	Discussion	
12:00 p.m.	Working Luncheon	Arapahoe Room
2:00 p.m.	Session IX, Summary of Group Discussions	Arapahoe Room
3:00 p.m.	Closing Remarks	F. Garnier J. S. Connolly

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PARTICIPANTS

Prof. Allen J. Bard
Department of Chemistry
University of Texas
Austin, TX 78712

Dr. Jacques Breton
Service de Biophysique
Commissariat a l' Energie Atomique
Centre d' Études Nucléaires
de Saclay, BP2
91190 Gif-sur-Yvette, France

Prof. Warren Butler
Department of Biology
University of California
La Jolla, CA 92097

Dr. John S. Connolly (Cochairman)
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. Satyen Deb
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. Arthur J. Frank
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. Francis Garnier (Cochairman)
Laboratoire Photochimie Solaire
Centre National de la Recherche
Scientifique
2 rue H. Dunant
94 Thiais, France

Dr. Claude Gavach
Centre National de la Recherche
Scientifique
BP 5051
34033 Montpellier-Cedex, France

Dr. Charles Giannotti
Centre National de la Recherche
Scientifique
I.C.S.N
91190 Gif-sur-Yvette, France

Dr. Pierre Joliot
Centre National de la Recherche
Scientifique
Institut de Biologie Physico-Chimique
13 rue Pierre et Marie Curie
75005 Paris, France

Dr. Jean Lavorel
Laboratoire de Photosynthèse
Centre National de la Recherche
Scientifique
91190 Gif-sur-Yvette, France

Prof. Gerard Lepoutre
Université Catholique
13 rue de Toul
59045 Lille, France

Dr. Stephen Lien
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. Alec Moradpour
Laboratoire de Physique des Solides
Bâtiment 510
Université d' Orsay
91405 Orsay, France

Prof. George Murphy*
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. Arthur J. Nozik
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

*Sabbatical visitor from the University of Oklahoma, 1979-1980.

PARTICIPANTS (continued)

Prof. Anthony San Pietro
Department of Biology
Jordan Hall 138
Bloomington, IN 47401

Dr. Jean-Pierre Sauvage
Institut Le Bel
Université Louis Pasteur
67000 Strasbourg, France

Dr. Michael Seibert
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. James C. Smart
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. Norman Sutin
Department of Chemistry
Brookhaven National Laboratory
Upton, NY 11973

Dr. John A. Turner
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Dr. Paul Weaver
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Prof. David Whitten
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Prof. Ferd Williams
Department of Physics
University of Delaware
Newark, DE 19711

CONCLUSIONS OF THE VISIT OF P.RAPPAPORT TO C.N.R.S (France)

3 - 6 OCTOBER 1978

Dr. Paul RAPPAPORT, Director of "Solar Energy Research Institute" (S.E.R.I), Denver, Co., has spent four days in France at the invitation of "Centre National de la Recherche Scientifique" (C.N.R.S). He met Professor Robert CHABBAL, General Director of C.N.R.S, Professor Henry DURAND, President of "Commissariat à l'Energie Solaire" (COMES) and Doctor Michel RODOT, Director of the Solar Energy Research Program in C.N.R.S (P.I.R.D.E.S). He also visited two C.N.R.S laboratories one laboratory of "Institut National de la Recherche Agronomique" (I.N.R.A) and the "Laboratoire d'Electronique et de Physique Appliquée" (L.E.P)

During these conversations and visits it became apparent that S.E.R.I and C.N.R.S have common interest in establishing cooperation which could include the following activities :

a) Exchange of visiting scientists

b) Exchange of information on programs

c) Joint seminars and workshops

d) Joint research programs

The wish was also expressed by M.DURAND and M.RAPPAPORT that a link be established between the data bank of S.E.R.I and the information center on solar energy at Perpignan (France), and that the development of this action be further studied by correspondence between them.

For the development of the proposed program (a) to d) above) between C.N.R.S and S.E.R.I, it was concluded that specific projects will be studied within the framework of the usual procedures of both agencies. The first project that will be considered is that of a joint seminar on solar photochemistry and photobiochemistry.

P.RAPPAPORT
Director of S.E.R.I

M.RODOT
Director of P.I.R.D.E.S

6 - 10 - 1978