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Solar Energy Materials and Solar Cells 38 (1995) 543–554

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Solar Energy Materials  
and Solar Cells

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## The photochemical conversion and storage of solar energy: An historical perspective

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### Abstract

The International Conference Series on *The Photochemical Conversion and Storage of Solar Energy* (IPS) is surveyed from an historical perspective over all the conferences (including IPS-0) extending back to 1974. Each of nine themes is explored as it has developed (or not developed) and discussed in the context of possible applications to solar energy conversion and storage and to other non-solar applications. Finally, an assessment is made of each theme as to its importance (a) for fundamental studies, (b) for solar applications and (c) for other non-solar applications.

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The first International Conference in this series (IPS-1) was held 24–28 August 1976 in London, Ont., Canada. There was an earlier Workshop on “The Current State of Knowledge of Photochemical Formation of a Fuel”, organized by Prof. Norman N. Lichtin and held in 1974 in Boston, which is now referred to as “IPS-0”. The complete list of the IPS Conferences and their organizers is given in Table 1.

The “IPS” acronym was introduced by Prof. Hiroshi Tsubomura in 1984. Hardly anyone knows precisely what it stands for (probably International Photochemical Storage), but it is a useful shorthand for the long title “International Conference on the Photochemical Conversion and Storage of Solar Energy” of this conference series.

I have been asked to prepare this historical perspective of all of the IPS Conferences up to IPS-9. This discourse is not meant to be a comprehensive review, but rather it is a very personal overview. I know that I run the risk of offending some people because I did not mention their work or because I did not include or emphasize a particular topic. No offense is intended, and I apologize in advance for any bias that may have crept into this account.

Table 1  
IPS Conferences and their organizers

Conf.	Place	Dates	Organizer(s)	Ref.
IPS-0	Boston, Mass., USA	September, 1974	Norman N. Lichtin	[1]
IPS-1	London, Ont., Canada	August, 1976	James R. Bolton and Morton Z. Hoffman	[2]
IPS-2	Cambridge, U.K.	August, 1978	Mary D. Archer	[3]
IPS-3	Boulder, Colo., USA	August, 1980	John S. Connolly	[4]
IPS-4	Jerusalem, Israel	August, 1982	Joseph Rabani	[5]
IPS-5	Osaka, Japan	August, 1984	Hiroshi Tsubomura	[6]
IPS-6	Paris, France	August, 1986	Jean-Marie Lehn and René Bensasson	[7]
IPS-7	Evanston, Ill., USA	August, 1988	James R. Norris and Dan Meisel	[8]
IPS-8	Palermo, Italy	July, 1990	Ezio Pelizzetti and Mario Schiavello	[9]
IPS-9	Beijing, China	August, 1992	Zhao Wu Tian and Yi Cao	[10]
IPS-10	Interlaken, Switzerland	July, 1994	Gion Calzaferri	

The genesis of IPS-1 occurred in the summer of 1975 when several delegates at a photochemistry conference in Edmonton met informally to discuss the organization of an international conference on the photochemical conversion and storage of solar energy. It was decided to hold it in London, Canada in August of 1976 with myself as the Organizer and Prof. Morton Hoffman from Boston University as the Co-organizer. The organization of the Conference was helped greatly by the background provided by the Workshop on "The Current State of Knowledge of Photochemical Formation of Fuel" (IPS-0), and both Prof. Norman Lichtin and Prof. Morton Hoffman helped greatly in suggesting speakers and other organizational details, such as raising money!

The IPS-1 Conference was a great success (175 delegates from 26 countries), and it was decided to hold repeat conferences every two years. The continuing International Organizing Committees have assured that the Conference has indeed been repeated every two years and has been a success every time. Now 18–20 years later we are at IPS-10, and it is my job to assess where we have come from, where we are at now and what the future may hold.

I debated as to how to organize this talk. One way would have been to discuss each conference in chronological order, but I have decided against that and instead have chosen to discuss specific topics or themes and how they have developed (or not developed) over the years. I begin with an overview and then discuss each theme in more detail.

## 1. Overview

To quote Prof. Norman Lichtin in the preface to the IPS-0 Proceedings, "The possibility of utilizing the sunlight which reaches the earth's surface each day as a

practical source of energy is a major challenge to modern science and technology. Photochemistry, a highly active area of both basic and applied research, offers an obvious potential route to practical use of solar energy.” The move to explore photochemical methods for the conversion and storage of solar energy was part of the general search for alternative energy sources following the oil crises of the early 1970’s. With photosynthesis as a practical example of the success of this approach, many scientists began a search, involving both practical and fundamental work, of practical schemes toward this goal. One indication of the importance of this field in science is that five Nobel Prize winners have given plenary lectures at IPS Conferences (Prof. M. Calvin — IPS-0, IPS-3; Prof. J.-M. Lehn — IPS-3; Lord G. Porter — IPS-4; Prof. R.A. Marcus — IPS-6; Prof. J. Deisenhofer — IPS-7), and only two of them had the prize at the time they gave their respective lectures.

The major themes explored in the IPS Conferences have been:

- (1) Molecular Photochemical Storage Systems
- (2) Photosynthesis
- (3) Photoinduced Electron Transfer (PET)
  - a. Theory of PET reactions.
  - b. Synthesis and PET properties of both inorganic and organic linked donor–acceptor molecules.

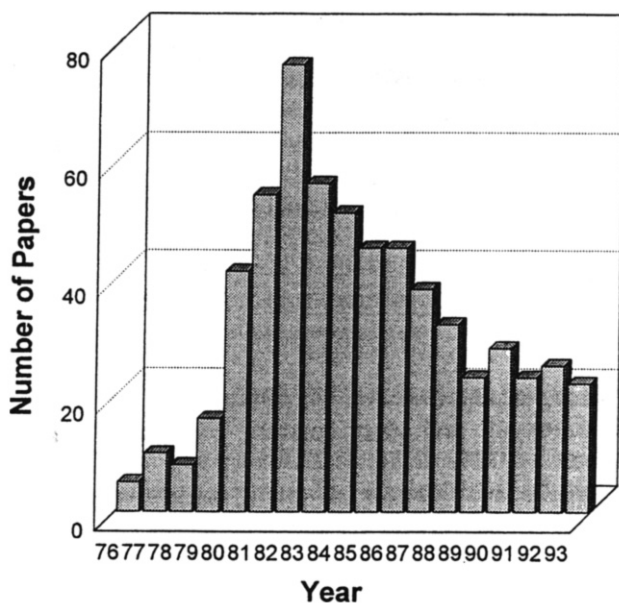


Fig. 1. Histogram of the number of papers by year with the key word “solar energy” in the RCDC Radiation and Photochemistry Database maintained by the Radiation Laboratory, University of Notre Dame, Notre Dame, IN.

- c. PET in membranes, micelles, polyelectrolytes and monolayers.
  - d. PET in natural and modified biological membranes, including reaction center proteins.
- (4) Fuel-producing Photochemical Redox Reactions
  - (5) Photogalvanic Cells
  - (6) Semiconductor Photoelectrochemical Cells (PECs)
    - a. Regenerative or photovoltaic cells
    - b. Photoelectrosynthetic or storage cells
    - c. Photocatalytic cells
  - (7) Microheterogeneous Systems
  - (8) Detoxification Processes
  - (9) Other Systems

Interest in this field underwent a marked increase from 1976 to 1982, followed by a decrease to what appears to be a mature steady state. This is illustrated in Fig. 1, where the number of papers coded with the keyword “solar energy” found in the Notre Dame Radiation Lab RCDC Database are plotted versus year.

## **2. Molecular photochemical storage systems**

This was one of the early themes and looked quite promising at the time. Sasse [IPS-1, p. 228] illustrated how one should seek endothermic organic photochemical reactions that can store some of the excitation energy in the products. This energy can then be released later as heat as the reaction is reversed [Jones et al., IPS-2, p. 1]. For a few years this stimulated some interesting organic photochemistry resulting in some innovative reactions, the best being Yoshida's [IPS-5, p. 27] substituted norbornadiene conversion to the corresponding quadricyclane; however, it is now recognized that the problems of limited energy storage efficiency and poor cycling stability have placed this option very low in priority. It is very difficult to compete economically with thermal solar collectors using water or rocks for heat storage.

## **3. Photosynthesis**

The photosynthesis reaction, driven by sunlight, consumes water and carbon dioxide to produce oxygen and plant matter. The stored solar energy in this “biomass” represents ~ 0.1% of the total annual solar energy reaching the Earth and is over 10 times the total amount of energy consumed by human activities in one year [Hall, IPS-1, p. 27]. Indeed Hall [IPS-6, p. 180] pointed out that biomass represents ~ 14% of the energy sources used worldwide and ~ 43% of the energy sources used in the developing countries. Thus photosynthesis is the most successful of any of the processes for the photochemical conversion and storage of solar energy. In 1976 it was known that the mechanism involves two photosystems acting in series and that each photosystem is activated by a reaction center protein.

However, not much was known about the structure or function of these proteins. Then in 1984 we awoke to the incredible images of the detailed crystal structure of the reaction center protein of the bacterium *Rhodospseudomonas viridis* [see Deisenhofer and Michel, IPS-7, p. 234], which confirmed the existence of the “special pair” of bacteriochlorophyll molecules first proposed by Norris, Katz and coworkers [11]. This unlocked Nature’s secret as to how light energy could be absorbed and part of it stored in the chemical energy of the products.

But the images were not enough — there were still many questions: What is the role of the backbone amino acids? What function does the intermediate bacteriochlorophyll molecule play? Why a dimer? Why is only one side functional? Much research ensued aimed at answering these and other questions. This has involved theoretical studies, genetic modifications [e.g., Wang et al., IPS-9, p. 9] sophisticated spectroscopic techniques and molecular models. It has even proven possible to force photosynthetic organisms to carry out a different photochemical energy storage reaction, such as the generation of hydrogen and oxygen from water, as shown by Greenbaum [IPS-6, p. 188]. Also other parts of the photosynthetic apparatus, such as the manganese-containing water-splitting enzyme [de Paula et al., IPS-6, p. 106], have had their structure and mechanism exposed in these Proceedings. Today the picture of the photosynthetic apparatus is much clearer, but many questions are yet to be answered.

#### 4. Photoinduced electron transfer (PET)

Since the primary photochemical reaction of photosynthesis involves photoinduced electron transfer (PET) reactions, there naturally has been a great deal of interest in building electron transfer models and in the theoretical understanding of the factors that influence PET. Even the idea of a “synthetic leaf cell” was expounded [Katz as cited by Stein, IPS-1, p. 15].

PET is involved in three types of reaction [Balzani and Scandola, IPS-3, p. 105]: exergonic photochemical reactions where light effectively lowers the activation energy, endergonic photochemical reactions where part of the excitation energy is stored in the electron transfer products and chemiluminescent reactions where reverse electron transfer reactions create excited states which then luminesce.

The idea of covalently linking a donor and acceptor to create a molecular model for studying PET goes back to the late 1970’s [Loach as cited by Connolly, IPS-4, p. 185]. Most early models were based on a porphyrin as the donor and a quinone as the acceptor. These and other similar systems, such as those introduced by Paddon-Row, Warman and co-workers and Closs, Miller and co-workers [Miller, IPS-6, p. 85] proved to be excellent ones for testing the predictions of the Marcus electron transfer theory, particularly the prediction that the rate of electron transfer as a function of increasing exergonicity should at first increase to a maximum and then decrease in the so-called “inverted region”. Several systems proved beyond doubt [e.g., Miller, IPS-6, p. 87] that the inverted region does exist and thus validated Marcus’s predictions made some 30 years earlier.

There was much interest in how an electron travels from donor to acceptor and the role of the structure of the linkage. A superexchange model [Miller, IPS-6, p. 85] proved popular but other models have also been proposed.

Since the reaction-center protein involves several electron-transfer components allowing the electron to transfer over a distance of about 20 Å, models have been built to incorporate multiple components. These have included triads [Gust, Moore and Moore, IPS-9, pp. 114–115], tetrads [Gust, Moore and Moore, IPS-9, p. 116] and even pentads [Gust, Moore and Moore, IPS-9, p. 118]. One must salute the artistry of the synthetic organic chemists who have built these beautiful compounds. Not to be outdone, the inorganic chemists have also synthesized impressive “supramolecular structures” [e.g., Denti et al., IPS-8, p. 31], as these are now called.

The knowledge gained from the intense research on PET has found application in other areas, such as the enhancement of the sensitivity of biological sensors [Heller, IPS-8, p. 73] and in transferring electrons across membranes [Seta et al., IPS-9, p. 78]. Monolayer structures have been used to study PET [Kuhn, IPS-2, p. 116], to show that the rate of electron transfer is an exponential function of distance between the donor and acceptor [Kuhn, IPS-2, p. 123] and to fabricate devices based on monolayer techniques [Fujihira, IPS-9, p. 197].

The study of PET reactions is not only important from a fundamental standpoint, but also has very significant potential applications. I think this is true particularly in the fields of photosensors and “molecular electronics”, the latter requiring electronic components that can transfer electrons over molecular distances (i.e., nm).

## **5. Fuel-producing photochemical redox reactions**

The prospect of using solar energy to generate a fuel, such as hydrogen from water or methane from carbon dioxide, has excited scientists in this field very much and has led to a wealth of papers. This has sometimes led to over-enthusiasm as illustrated by the stir created at the IPS-1 conference with the announcement by Sprintschnik et al. [IPS-1 Abstracts] that they were able to detect hydrogen and oxygen in a 2:1 ratio from monolayers of a ruthenium complex immersed in water. It later proved that this work could not be repeated.

One of the difficulties with a reaction such as the conversion of water to hydrogen and oxygen is that this is a four-electron process; whereas, photoredox reactions are almost always one-electron transfer reactions. Lehn [IPS-3, p. 164] has pointed out that one must avoid going through the radical intermediates because this would involve wasting energy in creating these radicals which are themselves also highly reactive and non-specific. Redox catalysts are required, such as Pt for electrons and RuO<sub>2</sub> for holes, to store redox equivalents so that hydrogen and oxygen can be evolved in concerted reactions [Grätzel, IPS-3, p. 151].

A theoretical analysis of the water decomposition reaction [Bolton, Haught and Ross, IPS-3, p. 327] indicates that for solar irradiation, the wavelength maximum

for a one- photosystem reaction (one photon per hydrogen molecule) is 778 nm and for a two-photosystem reaction, it is 1352 nm. Real systems will probably operate at wavelength maxima significantly shorter than these theoretical limits. This indicates that good efficiencies will probably be obtained only with double-photosystem schemes, a reduction photosystem for the generation of hydrogen and an oxidation photosystem for the generation of oxygen.

Many molecules have been used as light absorbers; however, the most popular have been ruthenium trisbipyridyl [ $\text{Ru}(\text{bpy})_3^{2+}$ ] and its variants [Balzani and Scandola, IPS-3, p. 101].  $\text{Ru}(\text{bpy})_3^{2+}$  absorbs well out into the visible ( $\sim 600$  nm), the excited state is both a strong reducing agent and a strong oxidizing agent and the molecule is not subject to serious side reactions. Usually sacrificial donors or acceptors are used so that the reduction or oxidation half reactions can be studied separately.  $\text{Ru}(\text{bpy})_3^{2+}$  has been used in both half reactions [Lehn, IPS-3, p. 171, 178]. In a few cases, the two half reactions have been coupled together [Lehn, IPS-3, p. 181]; however, efficiencies have been very low.

Probably the biggest problem facing the efficient production of a fuel using photochemical redox reactions is the ubiquitous back reactions. Several schemes have been developed to minimize the effect of back reactions. For example, Matsuo [IPS-5, p. 41] developed a clever scheme based on a redox polymer which allowed the photogenerated reduced species to move quickly along the polymer chain and so be removed from the donor site before recombination could occur.

The  $\text{Ru}(\text{bpy})_3^{2+}$ /methylviologen/EDTA/Pt reduction half reaction has probably been the most studied of all. Quantum yields and pH dependence are among the many factors studied [Amouyal and Koffi, IPS-5, p. 233]. The oxidation half-reaction has been less well studied; Calzaferri [IPS-9, p. 145] has shown that oxygen is evolved when a silver zeolite is irradiated in the presence of water.

The ultimate goal of these studies is the complete conversion of water to hydrogen and oxygen without the consumption of sacrificial agents. In writing this lecture, I had written that “to date this remains to be achieved, at sustained levels and at reasonable efficiencies, for systems in homogeneous solution with particulate redox catalysts.” However, I may be in error. Vrachnou and her colleagues have developed a system [12] that appears to split water photocatalytically without the consumption of any sacrificial agent and with an efficiency of almost 4%. The system involves a ligated tungsten complex that apparently is able to function as both a reduction catalyst to generate hydrogen and an oxidation catalyst to generate oxygen. If the past experience is to be a guide, one should not get too excited about these reports until they are confirmed in other laboratories.

## 6. Photogalvanic cells

Photogalvanic cells represent the first of two topics that explore the coupling of light absorption to the generation of electrical current and potential. It was first introduced to the IPS series by Lichtin [IPS-1, p. 119]. To quote Archer and Ferreira [IPS-3, p. 201], photogalvanic cells are photoelectrochemical devices “in

which a homogeneous photochemical reaction, nearly always electron transfer, yields electroactive products which can diffuse to, and react at, conventional electrodes." The study of such devices was a major topic at the early IPS conferences [e.g., Albery and Foulds, IPS-2, p. 41]. Archer and Ferreira [IPS-3, p. 207] showed that in only two of the four possible cell types could one hope to have any significant efficiency: a concentration cell, in which light causes a gradient in the concentration of an electrode-active component between two identical electrodes, and a differential cell, in which light causes changes in the concentrations of components of two redox couples, for which each electrode is selective to only one redox couple.

In spite of the early work in this field, research has now almost completely died out, probably due to the masterful analysis of Archer and Ferreira [IPS-3, p. 223], and I quote "... even if a cell of several percent efficiency were to be developed, degradation resulting from oxygen ingress, photochemical side-reactions and electrode aging remains a disturbing probability. Perhaps the most damaging aspect is that a successful photogalvanic cell will not meet an unsatisfied need, but will be in competition with solid-state photovoltaic cells, which transduce solar to electrical energy with proven reliability and performance. All in all, it must be admitted that photogalvanic cells, like Thursday's child, have far to go if they are to develop into cost-effective devices for conversion of solar energy".

## 7. Semiconductor photoelectrochemical cells (PECS)

One can trace the beginning of the excitement for the photochemical conversion and storage of solar energy to the announcement by Fujishima and Honda in 1971 that they had successfully split water in a photoelectrochemical cell (PEC) containing a titanium dioxide electrode and a Pt counter electrode. Although Gerischer [IPS-1, p. 95] pointed out that this cell was bias assisted, it nevertheless marked a very significant beginning.

Photoelectrochemical cells (PECs) are those in which light is absorbed by a semiconductor electrode or by a molecule adsorbed to such an electrode. PECs can be divided into three types [Bard, IPS-2, p. 64]: *regenerative or photovoltaic cells*, in which "the light which irradiates the semiconductor-solution interface is converted to electricity, ideally with no change in the composition of the solution or the semiconductor material"; *photoelectrosynthetic cells*, in which "light is used to drive the overall cell reaction in a non-spontaneous direction ( $\Delta G > 0$ ), so that radiant energy is stored as chemical energy (e.g., in fuels)"; *photocatalytic cells*, in which "a reaction is driven in a spontaneous ( $\Delta G < 0$ ) direction by the light energy. Here radiant energy is not converted to chemical energy but is used to overcome the energy of activation of the process".

*Regenerative or photovoltaic cells*: Efficiencies for the conversion of solar energy to electricity have been quite good, even in early work, such as the 6.6% achieved by Gerischer [IPS-1, p. 101] for a CdS electrode with a ferri-ferrocyanide redox



system in slightly acidic solution. Probably the most interesting PEC of this type is that of Grätzel [IPS-7, p. 294], consisting of a  $\text{TiO}_2$  cell coated with a ruthenium complex, where an efficiency of 12% was reported. However, here such devices are in direct competition with solid-state photovoltaic devices, where efficiencies approaching 30% [IPS-8, p. 587] have been achieved. It is not likely that PEC cells of this type will reach or surpass such efficiencies. However, there may be special applications for which PECs will be practical, especially if they can be manufactured at very low cost.

*Photoelectrosynthetic cells:* As with photochemical redox systems, the most studied reaction has been the conversion of water into hydrogen and oxygen as in the pioneering Fujishima and Honda cell. Progress has been impressive with an efficiency (for saved electrical energy) of 12% claimed by Heller [IPS-4, p. 67]. However, both the homogeneous photochemical redox systems and systems based on PECs suffer from comparison with a photovoltaic cell plus electrolyzer. As Gerischer prophetically noted [IPS-1, p. 109], “In my opinion, it seems to be more economic, even with the aim of photoelectrolytic generation of hydrogen, to concentrate on the development of a photovoltaic device as power source instead of performing this by direct photoelectrolysis. A conventional electrolysis cell for water decomposition has the advantage that in such a cell the overvoltage can be minimized by the use of catalytic electrodes for both electrode reactions and in addition to this one can collect the electrical current from a larger area of photovoltaic cells. The electrolysis can be performed at higher current density and the hydrogen can be generated more locally and even at higher pressure. Whether solid state photovoltaic devices are better or photoelectrochemical devices are better and more economical power sources for such an electrolysis will have to be learned in the future”. I think that the jury is still out on this question, but the photovoltaic cell plus electrolyzer system does set a benchmark against which photoelectrosynthetic hydrogen systems will have to be compared.

Another (perhaps more attractive option) is the photoelectroreduction of carbon dioxide to methanol or methane. This has been achieved [e.g., Fujishima and Hashimoto, IPS-9], but the efficiencies are still very low.

*Photocatalytic cells:* Not much has been reported in these Proceedings on this type of cell, except for some early work by Bard and his coworkers [IPS-2, p. 67] on photo-Kolbe reactions, in which carboxylic acids were decarboxylated to form hydrocarbons. More will be said on this type of reaction in microheterogeneous systems.

*Other PEC sub-topics:* The PEC topic has led to a wealth of fundamental studies ranging from theoretical analyses of the illuminated semiconductor/electrolyte interface [e.g., Gerischer, IPS-1, p. 77 and Memming, IPS-8, p. 193], hot-electron injection [Nozik, IPS-3, p. 276], the use of quantum-well structures [Nozik, IPS-9, p. 12] and studies of the mechanism of sensitized semiconductor electrodes [Willig et al., IPS-9, p. 130]. This fundamental work has led to a better understanding of this complex system and has opened the door to many applications [Heller, IPS-6, p. 187], such as improvement of pigments and paints, electronic and lightwave communication components, xerography and photosensors.

## 8. Microheterogeneous systems

Microheterogeneous systems are those in which light is absorbed by semiconductor particles in a suspension or on a supported structure. As Bard [IPS-2, p. 67, 68] noted: "The principles of photoelectrosynthetic and photocatalytic semiconductor cells can be extended to the design of particulate systems for carrying out the desired reactions. For example, a particle of  $\text{TiO}_2$  with some Pt deposited on it can be thought of as a short-circuited PEC cell, where the desired overall reaction occurs by electron and hole transfer at two sites on the particle".

Again one of the major themes has been the water to hydrogen and oxygen reaction. There was a lot of excitement about the evolution of hydrogen and oxygen on a single modified  $\text{TiO}_2$  particle [Grätzel, IPS-3, p. 153]; however, attempts to reproduce this work have not shown much success.

An exciting fundamental development has been the study of quantum-sized particles, where as the diameter of the particle is reduced, the bandgap increases and structure begins to appear in the absorption spectra [Brus, IPS-6, p. 126].

## 9. Detoxification processes

The use of solar energy to bring about the destruction of pollutants in contaminated waters and hence to detoxify them has been a late-developing theme in these Conferences. It first appeared as a significant theme in IPS-8 [e.g., Matthews, IPS-8, p. 427 and Zepp, IPS-8, p. 497], but hints of its importance appear as early as IPS-1, when Stein [IPS-1, p. 21] pointed out that the photochemistry of iron(III) hydroxide complexes leads to the generation of hydroxyl radicals.

The major thrust of this topic is to seek photochemical reactions that produce highly reactive radicals, such as the hydroxyl radical, which can then attack and destroy organic contaminants. These processes (called Advanced Oxidation Processes) are already a commercial reality in the treatment of waste waters using artificial UV lamps; however, the use of solar energy to achieve the same end has only been of recent interest. Nevertheless, it appears that photochemical reactions of this type are prevalent in Nature [Zepp, IPS-8, p. 506].

Until very recently, most of these studies have focused on  $\text{TiO}_2$  (in its anatase crystalline form) as a particulate photocatalyst (this is a sub-topic of microheterogeneous systems).  $\text{TiO}_2$  absorbs sunlight out to 385 nm and produces hydroxyl radicals on the surface by excess holes in the valence band oxidizing surface-bound hydroxyl ions. The overall performance of such solar detoxification systems has been modest, particularly since only  $\sim 3\%$  of the solar spectrum is absorbed by  $\text{TiO}_2$ , and the quantum yield for production of hydroxyl radicals is at most  $\sim 5\%$ . Nevertheless, there has been considerable interest in this option, including a field-scale demonstration using parabolic trough solar collectors [Pelizzetti et al., IPS-9, p. 217]. Serpone et al. [IPS-9, p. 33] presented an excellent overview of  $\text{TiO}_2$  photocatalytic systems for water treatment.

Another option for solar detoxification, which involves a homogeneous process, shows considerable promise [Bolton et al., IPS-10 Abstracts]. Here the absorber is  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ , which absorbs out to 500 nm and thus captures ~18% of the solar spectrum. This photochemical reaction produces  $\text{Fe}^{2+}$ , which couples with added hydrogen peroxide to produce hydroxyl radicals in a Fenton's reaction.

## 10. Other topics

Many other topics have been dealt with in these Proceedings, but I have time to mention only one, namely the theoretical limits on the efficiency of photochemical and photoelectrochemical solar energy conversion devices. I recall many hot debates as to what are the "thermodynamic" efficiency limits, especially the debate at IPS-3 that led to the Bolton, Haught and Ross paper [IPS-3, p. 297].

## 11. Prospects and conclusions

It now remains for me to sum up and gaze into the crystal ball as to what the future may hold. I have decided to do this by means of a table in which I outline my opinions as to the importance and possible future applications of each of the themes I have discussed. I realize that this is dangerous, as I am sure that I may upset some of you; however, for what its worth, my thoughts are summarized in Table 2. I have used a scale of *A–D*, where *A* means highly important, *B* means moderately important, *C* means marginally important, and *D* means no importance at all.

In conclusion, let me say that it has been a great experience reading back through all of the Proceedings. The writing in these volumes has been generally very good and the coverage excellent. For students of this field these Proceedings provide an excellent source of background information. As to overall prospects for this field, I have a feeling that after 20 years of study, which have been excellent

Table 2  
Prospects for the photochemical conversion and storage of solar energy

Topic	Importance for fundamental studies	Likely to lead to important new solar applications	Likely to lead to other non-solar applications
Molecular photochemical storage systems	<i>C</i>	<i>D</i>	<i>D</i>
Photosynthesis studies	<i>A</i>	<i>A</i>	<i>C</i>
Photoinduced electron transfer	<i>A</i>	<i>B</i>	<i>A</i>
Photochemical redox systems	<i>B</i>	<i>B</i>	<i>B</i>
Photogalvanic cells	<i>C</i>	<i>D</i>	<i>D</i>
Semiconductor photoelectrochemical cells	<i>A</i>	<i>B</i>	<i>B</i>
Microheterogeneous systems	<i>B</i>	<i>C</i>	<i>B</i>
Detoxification systems	<i>B</i>	<i>A</i>	<i>C</i>

and worthwhile, I have to conclude that although the scientific achievements have been outstanding, the practical achievements have been modest. Nevertheless, I believe that the solar photochemistry and photoelectrochemistry themes have provided a focus that has led to very significant increases in our understanding of electron-transfer reactions, photoprocesses at semiconductor/electrolyte interfaces and the design of impressive supramolecular structures not only to mimic the photosynthetic primary reactions, but also to provide the rudiments that may lead ultimately to true molecular electronic circuits. Thus, we need not apologize to *anyone* for the paucity of practical achievements. The advances in fundamental knowledge, in part stimulated by this conference series, could well lead to practical results that none of us would have predicted in 1976. But is this not just one of the characteristics of good science?

### Acknowledgements

I am grateful to the IPS Organizers who helped me to check the historical accuracy of this discourse. The Natural Sciences and Engineering Research Council of Canada provided financial support in the preparation of this paper.

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