CONF-780222--5

BIOMIMETIC APPROACH TO SOLAR ENERGY CONVERSION: ARTIFICIAL PHOTOSYNTHESIS

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Prepared for

5th Energy Technology Conference

Washington D. C.

February 26, 1978-March 1, 1978

U of C-AUA-USDOE

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BIOMIMETIC APPROACH TO SOLAR ENERGY CONVERSION: ARTIFICIAL PHOTOSYNTHESIS

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Unlike man-made devices for solar energy conversion, which use sunlight as a heat source or for direct conversion to electricity, green plants and certain bacteria use the energy of sunlight to drive chemical reaction that require an energy input in order to proceed in the desired manner. Thus, green plants use solar energy to convert carbon dioxide and water to carbohydrates, proteins, and lipids that are the nutrients for all other living organisms. Plants also produce natural fibers such as cotton and flax, polymers such as rubber; the energy required for these syntheses is supplied by the sun. The object of our solar conversion research and development program is to devise apparatus and systems for using solar energy for chemical purposes by methods that mimic those used by photosynthetic organisms. Sufficient progress has been made in the understanding of plant photosynthesis to make artificial photosynthesis a reasonable goal. Artificial photoreaction centers, the apparatus used by photosynthetic organisms for light energy conversion to chemical oxidizing and reducing capacity, have been made in the laboratory. Our synthetic reaction centers mimic with remarkable fidelity the properties of their in vivo prototypes. Some of the formidable problems that must still be solved and the future prospects for biomimetic devices for solar energy conversion will be discussed.

INTRODUCTION

An explanation for an interest in solar energy is scarcely necessary these days. Even the obdurate recognize that in the long run solar energy may offer the only answer to the energy crisis that will sooner or later be precipitated by the exhaustion of accessible fossil fuels. All possible energy sources that can possibly fill the resulting void must be explored and added to our energy repertory. As our only truly renewable energy source, solar energy must occupy an important place in such considerations. Despite the enormous problems which must be solved before solar energy can make a substantive contribution to our energy requirements, we cannot avoid the desireability, indeed the necessity, to exploit solar energy in whatever ways we can.

The most important technologies that have up to now been considered for solar energy conversion are solar heating and direct conversion to electricity. These are clearly the first practical solar energy conversion techniques which will achieve large scale use. However, there are unconventional, less familiar, more challenging, but perhaps more rewarding routes to solar energy utilization. It is one of these, artificial photosynthesis by a biomimetic approach that is the subject of this paper.

The term biomimetic is a compound of *bio* meaning life or living organism (from the Greek *bios*, life) and mimetic, showing mimickry (from the Greek *mimesis*, to imitate): hence biomimetic, a method or procedure based on or derived from a living organism by imitation or mimickry. A "biomimetic" technology, then, is predicated on a translation or abstraction of a process used by a living organism for a similar end. At first sight such a proposition may seem strange. Much of the biology of the past century has been focused on the interpretation of biological structure and function in mechanistic terms of the kind used in physics and chemistry. Yet here we are proposing to invert the normal course of events and to use living organisms as the models for a technological development rather than to use the constructs of physics and chemistry as models for the explanation of biological phenomena. A brief discussion of the reasons for advocating such an approach would thus appear to be in order.

Biomimetic Technologies

Many of the remarkable feats that living organisms carry out routinely are still a mystery, but even for some of the most complex activities of these, the mystery is not as total as it was only a short time ago. The concerted efforts of scientists in the application of the physical sciences to the interpretation of biological phenomena have been in many instances amazingly successful. We can take the chemistry of intermediary metabolism as an example. The exceedingly complex systems of chemical reactions used by cells to extract energy from carbohydrate and to synthesize biopolymers have yielded up many of their secrets. While the individual chemical reactions used by a cell in its metabolic activities can often be interpreted in terms of ordinary physical organic chemistry, the network of chemical reactions taken as a whole differs radically from similar chemical reactions carried out in the laboratory or in industry. Chemical reactions in biological systems are almost always accelerated and directed by very specific catalysis called enzymes. Whereas chemists must generally use high temperatures, high pressures, and highly reactive chemicals to achieve their ends, reactions in a living cell proceed with great speed and extra-ordinary specificity at ordinary temperatures and under very mild conditions. In addition, metabolic and biosynthetic reactions are integrated and self-regulated in a way unknown in the laboratory. As our understanding of enzyme structure and function deepens, the prospects for carrying out complex series of chemical reactions rapidly and in high yield by mild biomimetic syntheses become brighter. (Immobilized natural enzymes now coming into use may be regarded as a way station.) In similar fashion, new insights into protein and biopolymer structure, molecular biology and the genetic code, and the structure and function of organelles such as mitochondria and chloroplasts will surely have practical consequences. We can look forward to nitrogen fixation by the methods of nitrogen-fixing microorganisms in leguminous root nodules, to fiber production by the techniques of the silk-worm or the cotton plant, to water desalination by the active-transport mechanisms of the kidney, to protein or biopolymer synthesis by the methods of the ribosome, and to biomimetic organic syntheses (cf. Tishler, 1977). We can expect from the neurological and brain function studies of today new departures in electronics and computers based on nerve function in the central nervous system. In brief, radically new and basically different ways of achieving technological goals by procedures that mimic those used by living organisms can be seen on the horizon. Biomimetic solar energy conversion may well be among the earliest to come into full view.

The necessary preliminary to a biomimetic technology is a sufficiently detailed understanding of the biological process that is to serve as the model. Obviously, if the essential features of the model are perceived incorrectly, there is no possibility of success. It thus becomes an exercise in judgement on the part of the investigator as to whether the process in Nature is sufficiently well-defined and understood to make for a successful abstraction from the model. For solar energy conversion, judged by the success already achieved in the

mimicking of an essential element of the light conversion apparatus of photosynthetic organisms, information adequate to justify a biomimetic approach to solar energy conversion already exists. Such enterprises as wood plantations and the generation of biomass make use of living photosynthetic organisms. These are interesting and valuable routes to solar energy utilization but their problems and goals are different from the biomimetic technologies for light energy conversion that we discuss here. We can now consider some aspects of photosynthesis pertinent to the development of biomimetic solar energy conversion technologies.

Green Plant Photosynthesis

Photosynthesis as carried out by green plants and certain bacteria is far and away the most important process that makes use of solar energy. The energy of sunlight, however, is not used by plants as a heat source or for direct conversion to electricity. Rather, photosynthetic organisms use solar energy for chemical purposes. The energy of sunlight is used by photosynthetic organisms to drive chemical reactions that do not proceed spontaneously and thus require an input of energy in order for the desired chemical reactions to occur. A biomimetic solar energy conversion process based on plant photosynthesis thus has as its objective the conversion of solar energy to chemical energy. Photosynthesis in Nature is a gigantic chemical operation. Every year about 200 billion tons of organic matter is produced by photosynthesis (Boardman, 1977). All of the energy required to produce this vast quantity of organic matter comes from the sun. Photosynthesis as carried out by green plants and photosynthetic bacteria appears to have had its origin on earth 3 to 4 billion years ago. Thus, photosynthetic organisms are not only the largest but they are also the most experienced users of solar energy. A good general introduction to photosynthesis can be found in a book by Rabinowitch and Govindjee (1969).

Photosynthesis ("synthesis with the help of light") converts purely inorganic compounds to organic matter. The process of photosynthesis is generally formulated as the reduction of carbon dioxide by electrons abstracted from water to form organic compounds containing carbon-hydrogen (C-H) bonds and molecular oxygen:

$$h\nu + CO_2 + H_2O \rightarrow \text{organic compounds} + O_2 \qquad (1)$$

This process as written is exactly the reverse of combustion, in which organic matter reacts with oxygen to form carbon dioxide and water:

$$\text{Organic matter} + O_2 \rightarrow CO_2 + H_2O + \text{Heat} \qquad (2)$$

Combustion of organic matter (coal, oil) produces large amounts of heat or energy and once initiated proceeds spontaneously. To reverse the process of combustion and to force the combustion products to recombine to form organic matter requires an energy in-put roughly equivalent to the amount of heat evolved in combustion. The energy required for the photosynthetic reversal of combustion comes from the energy of light quanta, symbolically $h\nu$ in Eq. (1).

Chlorophyll is universally acknowledged to be the primary photoreceptor in photosynthesis. The working element in the apparatus in which light energy is converted to chemical energy in photosynthetic organisms is chlorophyll. While there are other pigments (light absorbing compounds, auxilliary chlorophylls) normally present in or near the photosynthetic apparatus, the primary light conversion events in photosynthesis in many green plants involve only chlorophyll a, the chlorophyll present in all organisms without exception that evolve oxygen in photosynthesis. Two generations of research by physicists, chemists, plant physiologists, agronomists, botanists, electron microscopists, to name only some of the participants who have established a

number of widely accepted facts about chlorophyll function in photosynthesis that are highly relevant to our biomimetic goals. Chlorophyll function in light energy conversion, first of all, is a cooperative phenomenon. Perhaps as many as several hundred chlorophyll molecules act in unison to convert the energy of a single photon to an electron (chemical reducing power) and a positive charge (chemical) oxidizing power). The reductant and the oxidant created by light energy conversion are then used to drive chemical reactions, i.e., to reduce CO_2 and to oxidize H_2O. The large number of chlorophyll molecules whose cooperation is essential to light energy conversion are organized into a photosynthetic unit (PSU). While it was once considered that all the chlorophyll molecules in the PSU were all equivalent and served the same purpose, this is now realized not to be the case. The chlorophyll of the PSU has at least two well-defined functions that are carried out by specialized chlorophyll structures. The large majority of the chlorophyll molecules are used to collect light energy. Because they are used to collect electromagnetic radiation, the chlorophyll molecules used for harvesting light quanta are called antenna chlorophyll. When a chlorophyll molecule in the antenna absorbs a photon, that particular chlorophyll molecule is excited to a high-energy electronic state. By a complicated process of energy transfer, the details of which are still being debated, the excitation energy is transferred through the chlorophyll molecules of the antenna to a very few chlorophyll molecules where the excitation energy is trapped and light energy conversion occurs. The chlorophylls in which the conversion occurs are called photo-reaction center chlorophyll. About 99% of the chlorophyll in the PSU has an antenna function, the other 1% of the chlorophyll is organized into a photo-reaction center (s).

The difference between the antenna and the reaction center is not at the molecular level. Both are composed of the same chlorophyll. However, the building blocks are arranged in different ways to produce the specialized chlorophyll structures. It is not surprising therefore that antenna and reaction center chlorophyll in the intact photosynthetic organism have different physical properties appropriate to the different purposes they serve. Antenna and reaction center chlorophylls have different light absorption properties, with a reaction center chlorophyll absorbing light of longer wavelength than does the antenna. The reaction center is spoken of as having a visible absorption spectrum that is red-shifted relative to that of the antenna. More precisely, maximum absorption occurs in the red region of the visible spectrum in the antenna at 680 nm, whereas the reaction center in green plants is often referred to as P700 (where P stands for pigment). The reaction center in photosynthetic bacteria is by the same system designated P865.

Two circumstances have made progress in the interpretation of reaction center structure and function more rapid than for antenna. In green plants light absorption by the reaction center can no longer be observed when the plant is carrying out photosynthesis. When the plant (or chloroplast) returns to the dark, light absorption at 700 nm is restored. P700 evidently undergoes some kind of a (reversible) photo-bleaching when carrying out solar energy conversion. Consequently reaction center function was early described as a photo-oxidation in which an electron is ejected from the reaction center:

$$P700 + h\nu \rightarrow P700^{+\cdot} + \varepsilon \ . \qquad (3)$$

The ejection of an electron from the chlorophyll in the reaction center leaves the reaction center with a positive charge. P700 and $P700^+$ are different chemical species with different light absorption properties and this manifests itself by the disappearance of the P700 absorption as $P700^+$ is formed. The ejection of one electron from P700 has another important consequence. Most organic compounds have an even number of electrons, which are paired in groups of two. Removal of one electron leaves an odd number of electrons, with one electron unpaired. Compounds containing an old number of electrons are known as free radicals,

and these have an interesting property that makes them easy to detect and follow. The spectroscopic technique of electron paramagnetic resonance (epr) is an exceedingly sensitive tool for the detection of free radicals. Barry Commoner and his colleagues (1956, 1957) were the first to detect the formation of chlorophyll free radicals in the primary events of photosynthesis. Subsequent work has shown that the photo-bleaching of P700 is concomittant with the formation of a free radical. Careful measurements have shown that for each photon that reaches the trap, one P700 is bleached and one $P700^{\dagger}$ and an electron are produced. The rate of bleaching of P700 and of the formation of $P700^{\dagger}$ are within experimental error identical. A very similar process occurs in photosynthetic bacteria. P865 is also photo-bleached on irradiation with light and forms the free radical $P865^{\dagger}$ by ejection of an electron. Again the photo-bleaching and the formation of the free radical are concomittant and proceed with the same kinetics. Again, one photon trapped by P865 produces within experimental error one electron.

The PSU has a number of other important components. The reaction center is spoken loosely as ejecting an electron, but free electrons (in the sense of electrons in a metallic conductor) are certainly not present in the photosynthetic organism. Ejection of an electron from the reaction center proceeds by transfer to an electron acceptor. As there is no metallic conduction at the molecular level, subsequent electron transfer to the reagent that reduces CO_2 is by a series of electron transfer agents, arranged so to speak in a bucket brigade that passes the electron along until it forms the chemical reductant that carries out the chemical reactions associated with photosynthesis. Similarly, another conduit exists along which an electron abstracted from water (in the case of green plants) is passed along to $P700^{\dagger}$ to restore it to its resting condition, thus making it available for another light conversion event. These electron transport conduits, which have been intensively studied in recent years, play a vital role in photosynthesis. The tendency to acquire and loose electrons (redox properties) must be very carefully graduated in the electron transport chain to make sure the electron proceeds in the desired direction. Any electron ejected from a reaction center that finds its way back to its origin means a wasted photon. Not only are the redox properties of the components of the transport chain important, but their spatial relationships are likewise crucial, for the distances and orientations must be matched to the redox properties to achieve the high degree of directionality essential for efficient operation. The electron conduits associated with the reaction center thus are a highly important part of the photo-conversion apparatus.

The auxilliary pigments that may be present in the PSU appear to be optional equipment for improving the efficiency of light harvesting and energy transfer. It may perhaps be worthwhile making explicit a point that has only been made implicitly. The chemical reactions of photosynthesis, the synthesis of carbohydrates, proteins, etc. from the reduction of CO_2, and the abstraction of electrons from water do not take place in the PSU. All of the chemical reactions of photosynthesis (the so-called dark reactions because they can proceed in the dark after light energy conversion) appear to occur in regions of the chloroplast or chromatophore (in bacteria) removed from the reaction center where the oxidizing and reducing power is generated. Once oxidizing and reducing power are produced, the particular chemical use to which they are put is at the discretion of the designer.

The photo-reaction center and its allied components in the PSU may be thought of as an electron pump powered by light. Low energy electrons are removed from water and pumped to an energy level sufficiently high to reduce CO_2. The electrons are flowing up-hill, and the energy input required for this process, which would not occur spontaneously, is derived from the energy of sunlight. A highly schematic representation of a photosynthetic unit is shown in Figure 1.

The Chlorophyll Special Pair

Until quite recently the presumption was that the primary electron donor in a particular light conversion event was a solitary chlorophyll molecule. This was certainly not an unreasonable assumption. However, this view cannot survive close inspection. Whereas reaction center chlorophyll, as indicated by its designation as P700, absorbs maximally at 700 nm, monomeric chlorophyll absorbs at ~660 nm; thus the light absorption properties of the two are so different as to preclude an identification of P700 as a single molecule of chlorophyll a. The epr data are also incompatible with such an identification. If careful attention is paid to the epr signals from $P700^{+\cdot}$ and Chl $a^{+\cdot}$ it can be seen that although the two signals are in general similar in shape, the signal from $P700^{+\cdot}$ is about 40% narrower than the one from Chl $a^{+\cdot}$. Clearly a chlorophyll species that with a red-shifted absorption spectrum and a considerably narrowed epr linewidth cannot be equated with Chl $a^{+\cdot}$. It is not surprising that earlier attempts to mimic P700 behavior with monomeric chlorophyll a were unsuccessful.

Laboratory studies on chlorophyll at Argonne National Laboratory (Norris et al. 1971) provided an important clue to the anomalous properties of P700. Chlorophyll a interacts with water in a hydrocarbon solvent to form chlorophyll-water adducts that optically are strongly red-shifted to 740 nm and turn out to be photo-active by the epr criterion when irradiated with red light. This chlorophyll-water adduct, which we may call P740, is a purely synthetic species that as far as we know is not of physiological significance. Its importance derives from its photo-activity. Of all the different chlorophyll species that can be formed in the laboratory, and by now there are scores, only P740 shows the property of photo-activity. Like P700, P740 ejects an electron to form $P740^{+\cdot}$, a free-radical species with a very characteristic and unusual epr signal. The unique feature of the $P740^{+\cdot}$ signal is its extreme narrowness, of the order of about one-tenth that of Chl $a^{+\cdot}$. The narrowing of the signal can be accounted for in a straightforward way that has been shown to be applicable in similar situations. Given a system composed of many molecules that are equivalent, an unpaired electron can migrate and occupy equivalent sites in anyone of the host molecules. If the rate of migration is sufficiently fast, an averaging process occurs that narrows the epr signal. In such a situation, the unpaired electron is effectively present simultaneous to a certain extent at all equivalent molecular sites. The unpaired electron is delocalized, in our particular case, over all the chlorophyll molecules in $P740^{+\cdot}$. The greater the extent of delocalization, i.e., the greater the number of chlorophyll molecules involved in electron-sharing, the narrower the line. As $P740^{+\cdot}$ obviously contains more equivalent chlorophyll molecules than does $P700^{+\cdot}$, its epr signal is narrower. The relationship between the linewidth and the number of chlorophyll molecules involved in the delocalization process is quantitative and the epr linewidth in this situation can thus be used to determine the number of chlorophyll molecules in the aggregate.

When such an analysis is applied to $P700^{+\cdot}$, a surprising fact emerges. The narrowing of the $P700^{+\cdot}$ epr signal relative to that of monomeric Chl $a^{+\cdot}$ can be accounted for with considerable precision by the assumption that the unpaired electron in $P700^{+\cdot}$ is shared by *two* chlorophyll molecules (Norris et al. 1971; Katz and Norris, 1973). In fact, for a large number of green plants and photosynthetic bacteria that have been examined by magnetic resonance, the epr signals can be accounted for to with a few percent by the postulate that pairs of chlorophylls are the primary electron donor in photosynthesis. This is equally true for green plants and for purple photosynthetic bacteria. The photo-reaction center except for the chlorophyll from which it is constructed appears to be essentially the same in green plants and in photosynthetic bacteria. To differentiate the pairs of chlorophyll that are the primary electron donors in light energy conversion from

other chlorophyll aggregates that may be present, they have been called chlorophyll special pairs, Chl_{sp}.

Synthetic Chlorophyll Special Pairs

Various structures have been proposed for the Chl_{sp} (Katz et al. 1977, 1978a,b). One of the more successful of these (in the sense of accounting for the optical and epr properties of P700) is that of Shipman et al. (1976) (Figure 2). In this structure for Chl_{sp}, two chlorophyll molecules are held together in a parallel orientation by two molecules of a cross-linking agent, which may be water, alcohol, or any one of a number of substances that interact with the central magnesium atom of chlorophyll and can hydrogen bond to an oxygen atom of the other chlorophyll molecule. In this structure, the two chlorophyll molecules are fully equivalent, hence electron delocalization can occur. The two chlorophyll molecules arranged as shown in Figure 2 are brought as closely together as possible; they are at the optimum distance for the electronic systems of the two chlorophylls to be just in contact, again facilitating electron sharing. The close proximity of the two chlorophylls leads to interactions between the electronic systems that should cause a red-shift in the visible absorption spectrum. Theoretical calculations predict that such a structure should indeed absorb light maximally at ∿700 nm. Thus the conceptual model for Chl_{sp} seems to have the properties of P700.

Fabricating such a structure in the laboratory is a challenge, but it is one that has been successfully met. In early efforts a chlorophyll species with the desired Chl_{sp} properties has been prepared at very low temperatures by strong cooling of a toluene solution containing the chlorophyll and ethyl alcohol. This synthetic Chl_{sp} has the proper visible absorption and epr properties, but it is awkward to work with in an organic glass at -100°C. The low temperatures are required to force the two halves of the synthetic Chl_{sp} to assemble themselves in the proper configuration. At room temperature, the two halves are more prone to diffuse away from each other than they are to combine. This tendency to drift apart at ambient conditions can be circumvented by linking the two halves of the Chl_{sp} chemically by a true chemical bond so that they cannot separate. A similar strategy has been used by Boxer and Closs (1976).

At Argonne National Laboratory, Dr. Michael R. Wasielewski (1976, 1977) has successfully surmounted the formidable chemical problems and has chemically linked two chlorophyll molecules or two bacteriochlorophyll molecules into the structure shown in Figure 3. The two parts of the Chl_{sp} can no longer diffuse away from each. When the linked chlorophylls are dissolved in a solvent such as benzene or carbon tetrachloride, and a substance such as water or alcohol added, the linked dimer folds and assumes the structure of Figure 2. That it in fact has the desired structure is verified by nuclear magnetic resonance spectroscopy, which provides convincing proof of structure. When the folded configuration is assumed, the visible absorption spectrum shifts to ∿700 nm. The folded linked dimer converted by oxidation to the Chl_{sp}^{+} free radical has the ability to share an unpaired electron, for its epr signal is almost indistinguishable from that of $P700^{+}$ in green plants. The properties of our synthetic Chl_{sp} thus faithfully mimic the optical and epr properties of in vivo green plant P700.

Light-Mediated Electron Transfer with Synthetic Chl_{sp}

Efforts to develop biomimetic devices for light-mediated electron transfer have been in progress at Argonne National Laboratory for several years. Light-mediated electron transfer has been studied (Katz et al. 1978b) in a cell consisting of two compartments separated by a semi-permeable membrane or a metal foil. Each of the two compartments has inserted into it a platinum electrode to monitor electrical events. The semi-permeable membrane or the foil has deposited upon it a film of our synthetic Chl_{sp} (or the photo-active P740 chlorophyll-water adduct). Light ejects an electron from the synthetic special pair, which is then taken up by the electron acceptor. To restore the Chl_{sp}^{+} to its original state, an electron from the donor compartment is used. An electron flow results, as evidenced by the appearance of an emf and current flow on light irradiation, which then decays when the light is turned off (Fig. 4). The synthetic Chl_{sp} thus shows the required ability to eject an electron when irradiated with light.

Problems and Prospects

We consider the simulation of the in vivo reaction center by the synthetic Chl_{sp} to be a significant step in the direction of a biomimetic technology for solar energy conversion, but only the first of the many that will need to be taken. An immediate objective must be to equip the synthetic Chl_{sp} with the highly directional electron conduits essential for efficient electron flow. It is such electron transfer chains that make the Chl_{sp} in vivo such an efficient device, for once an electron is ejected from the Chl_{sp}, the probability of its return is very small. To achieve this will require a program in molecular electronics and decisions whether efficient electron conduction will be by organic metals, one-dimensional electrical conductors, or the like, or by a biomimetic approach that seeks to simulate the electron transfer protein chains in the green plant chloroplast. The synthetic Chl_{sp} as it now stands has no antenna. Whether an antenna must be attached is not yet clear, but there may be good reasons to do so. In which case, we must proceed to synthesize and afix an antenna to the Chl_{sp}. As taxing as these tasks will be, they do not include the most important unsolved problem of them all. We believe that, at least in principle, we now have a good working hypothesis about that part of photosynthesis that is involved in the reducing side of photosynthesis. However, the problem of the oxidizing side of photosynthesis, the means by which electrons are extracted from water is essentially a mystery. Unless water is the ultimate source of the electrons used in reduction, there is no real point to biomimetic solar energy conversion. There is no concensus about the oxygen side of photosynthesis, and it is highly probable that important features of oxygen production in photosynthesis still remain to be discovered. To attain a sufficient understanding of oxygen production in green plant photosynthesis to make a biomimetic attack feasible will require a massive effort but the odds for success are all in its favor.

Only a few percent of the solar energy falling on a field over a growing season can be retrieved by combustion from the vegetation that grew there. To some, this argues for photosynthesis as an inefficient process. An energy balance sheet derived in this way, however, does not give an accurate picture of the situation. In the course of growth, for example, plants transpire enormous amounts of water, a process that requires a substantial energy input. There must be a large energy requirement for the synthesis of the highly ordered plants. Solar energy used for such purposes is not recoverable as heat of combustion. A Chippendale chair and an equal weight of wood from which the chair was made have the same heat of combustion, but clearly the energy input required to convert the wood to furniture cannot be negligible. The living plant uses solar energy for many purposes: to survive drought, to accomodate to extremes of heat and cold, to reproduce, to defeat predators, to compete for an ecological niche, and many more. A biomimetic technology for solar energy need not use energy for any of these. The conversion of solar energy to

chemical energy in the in vivo Chl_{sp} is essentially quantitative; every photon trapped by the Chl_{sp} produces one electron. The primary light conversion step in photosynthesis is highly efficient. It can be made as efficient in a biomimetic device, which in addition does not require for its own purposes the energy needed by a living organism. There is also no reason to suppose that in the long run that we cannot improve on nature. The chemical structure of chlorophyll is determined at least in part by the biosynthetic pathways available to the plant. Not all of the structural features of chlorophyll may be essential for its function in photosynthesis. Perhaps the Chl_{sp} might be more efficient at a different wavelength of light. It may well be that simpler, more rugged, and equally efficient chlorophyll analogs may be developed that will be better suited to solar energy conversion.

There is a natural curiosity as to what such a biomimetic solar energy conversion installation might look like and to what uses it might be put, which is shared by the writer. Depending on the situation at the time it might be a plant for producing hydrogen and oxygen by photolysis of water. Or, it might evolve into a rubber plantation without rubber trees. In whatever fashion biomimetic solar energy conversion materializes, one thing appears quite certain. A deep understanding of such an important solar energy conversion process as plant photosynthesis must inevitably have a major impact on the future use of solar energy.

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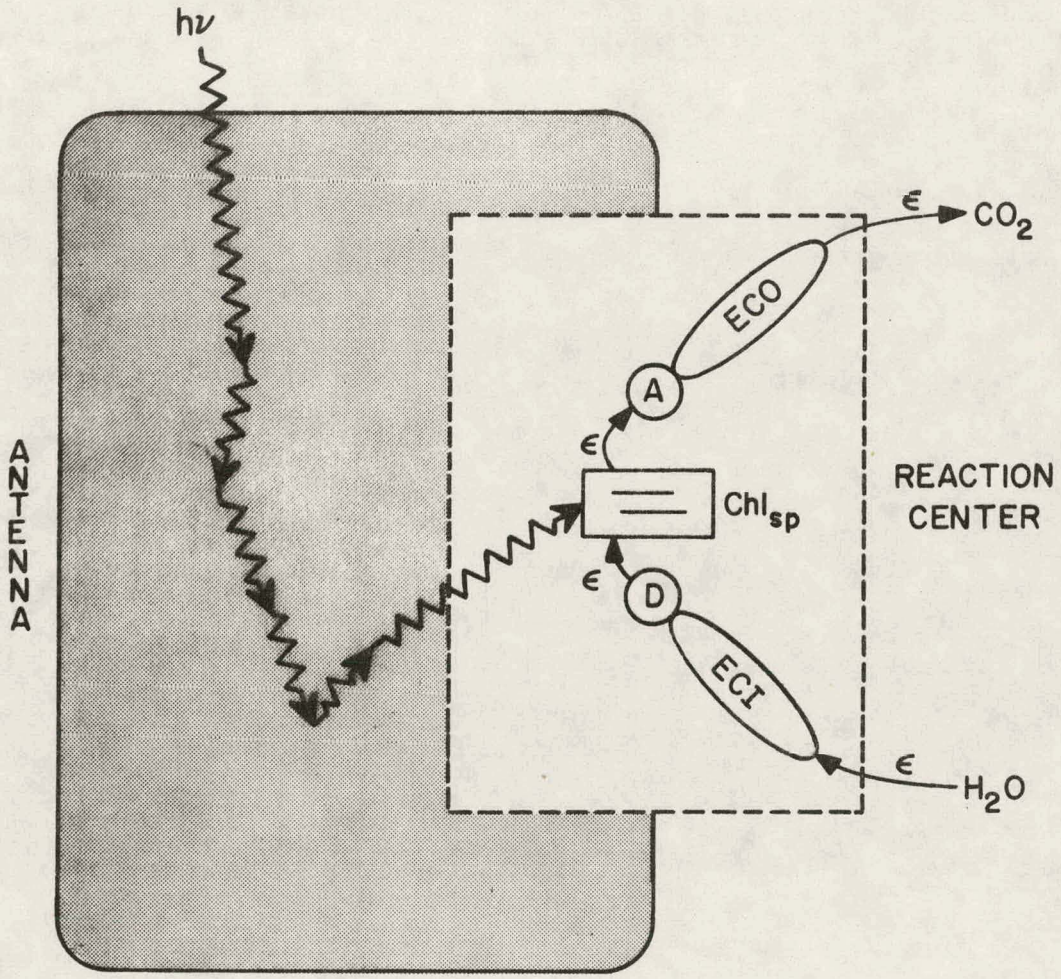
FIGURE LEGENDS

Figure 1. A highly schematic photosynthetic unit showing the course of events when a light photon is absorbed. , electron; ECI, electron conduit in; ECO, electron conduit out; Chl_{sp}, the reaction center; A, the primary acceptor; D, the primary donor to $Chl_{sp}^{\dagger}$. The orientation of the antenna chlorophyll molecules is purely arbitrary and does not necessarily imply the presence of monomer chlorophyll.

Figure 2. The Chl_{sp} model of Shipman et al. (1976). The two chlorophyll molecules are parallel and laterally displaced. The electron systems of the two chlorophylls are just in contact. The two halves can be linked by water, alcohol, or by any of a number of compounds that can coordinate to the magnesium atom and also form hydrogen bonds. The cross-linking agent in the in vivo Chl_{sp} is unknown, but may be water or side-chain groups in protein.

Figure 3. Synthetic covalently linked Chl_{sp} shown in its folded configuration. The chemical link is in the upper right. Except for the link, the structure is identical with that of Shipman et al. (1976) in Figure 2.

Figure 4. Photo-voltage produced by light irradiation of synthetic Chl_{sp}. The voltage and current flow are indicative of light-assisted electron transport. On and off indicate the light cycle. ASC, ascorbate, an electron donor; AQS, anthraquinone sulfonate, an electron acceptor. Both the donor and acceptor are in aqueous solution in a two compartment cell divided by a metal foil on which the synthetic Chl_{sp} is present as a film.



PHOTOSYNTHETIC UNIT

Figure 1

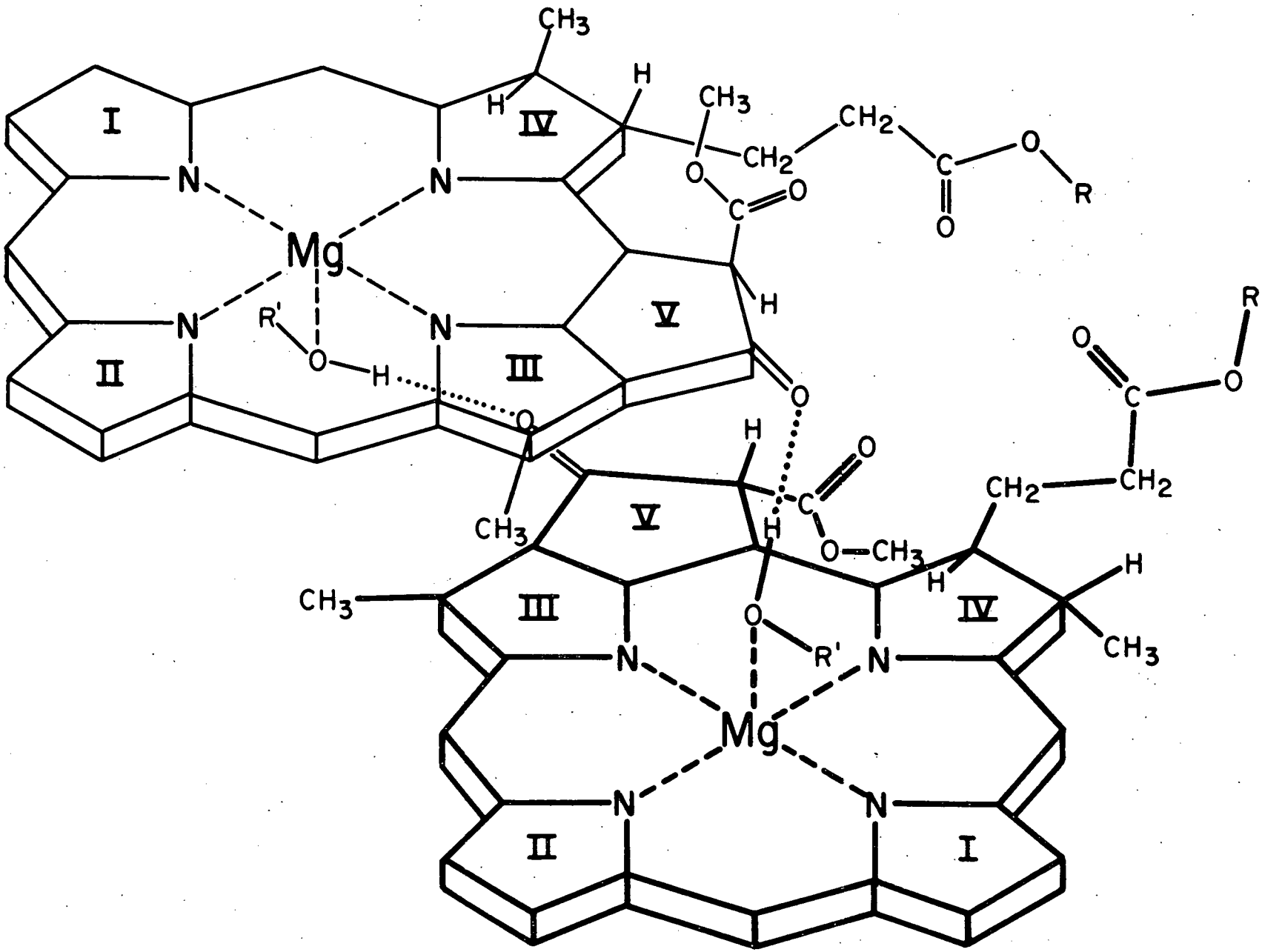

CH3
H
CH3
CH2
CH2
C
O
R
I
IV
N
N
Mg
R'
O
H
II
III
V
O
H
CH3
V
H
O
C
O
O—CH3
CH2
CH2
R
O
C
O
CH3
III
IV
H
CH3
O
R'
N
N
Mg
N
N
II
I

Figure 2

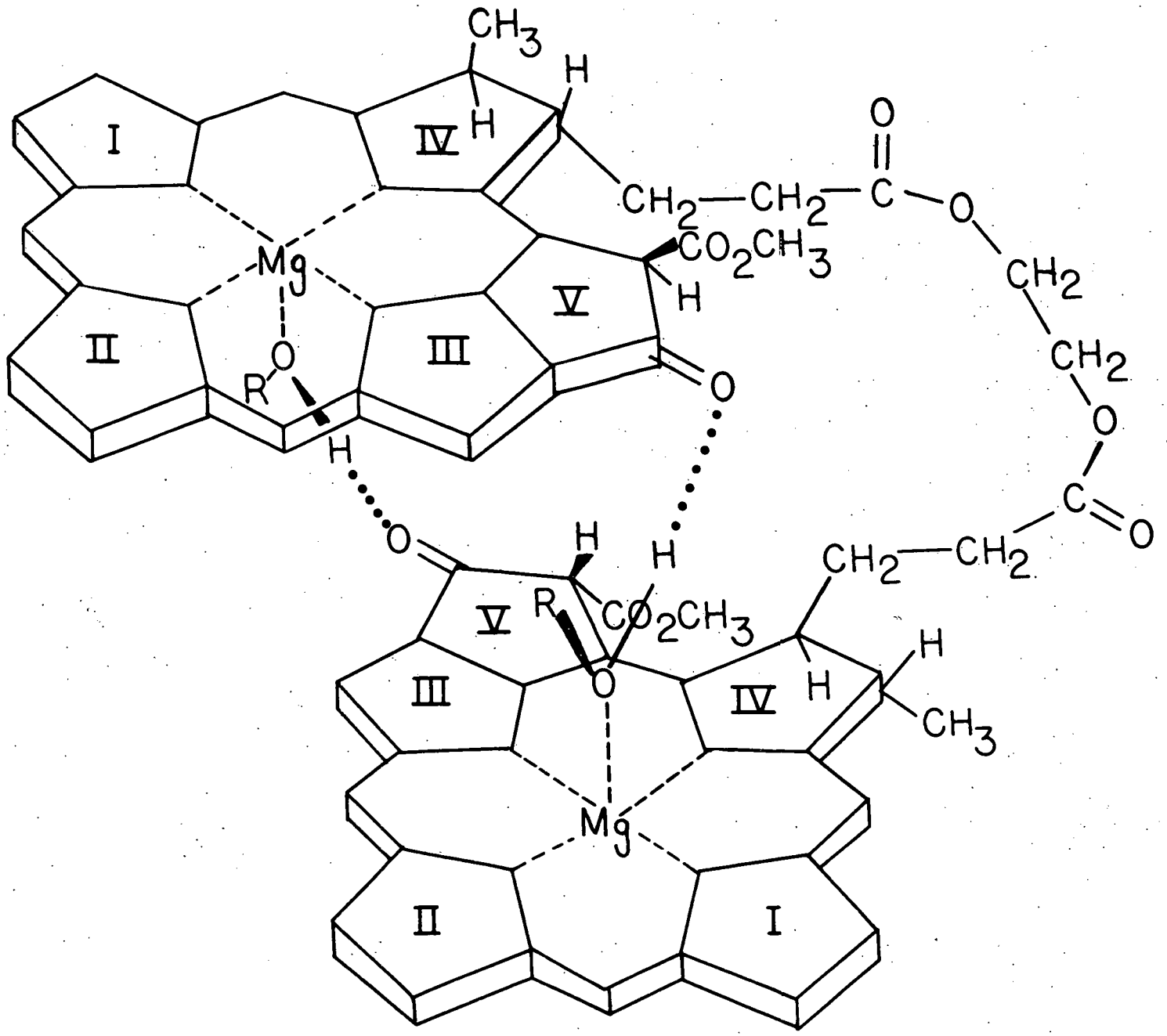

CH3
H
I
IV
H
CH2—CH2
C
O
O
CO2CH3
Mg
V
CH2
H
II
III
O
R
O
H
O
CH2
O
C
O
H
H
CH2—CH2
V
R
CO2CH3
H
III
O
IV
H
CH3
Mg
II
I

Figure 3

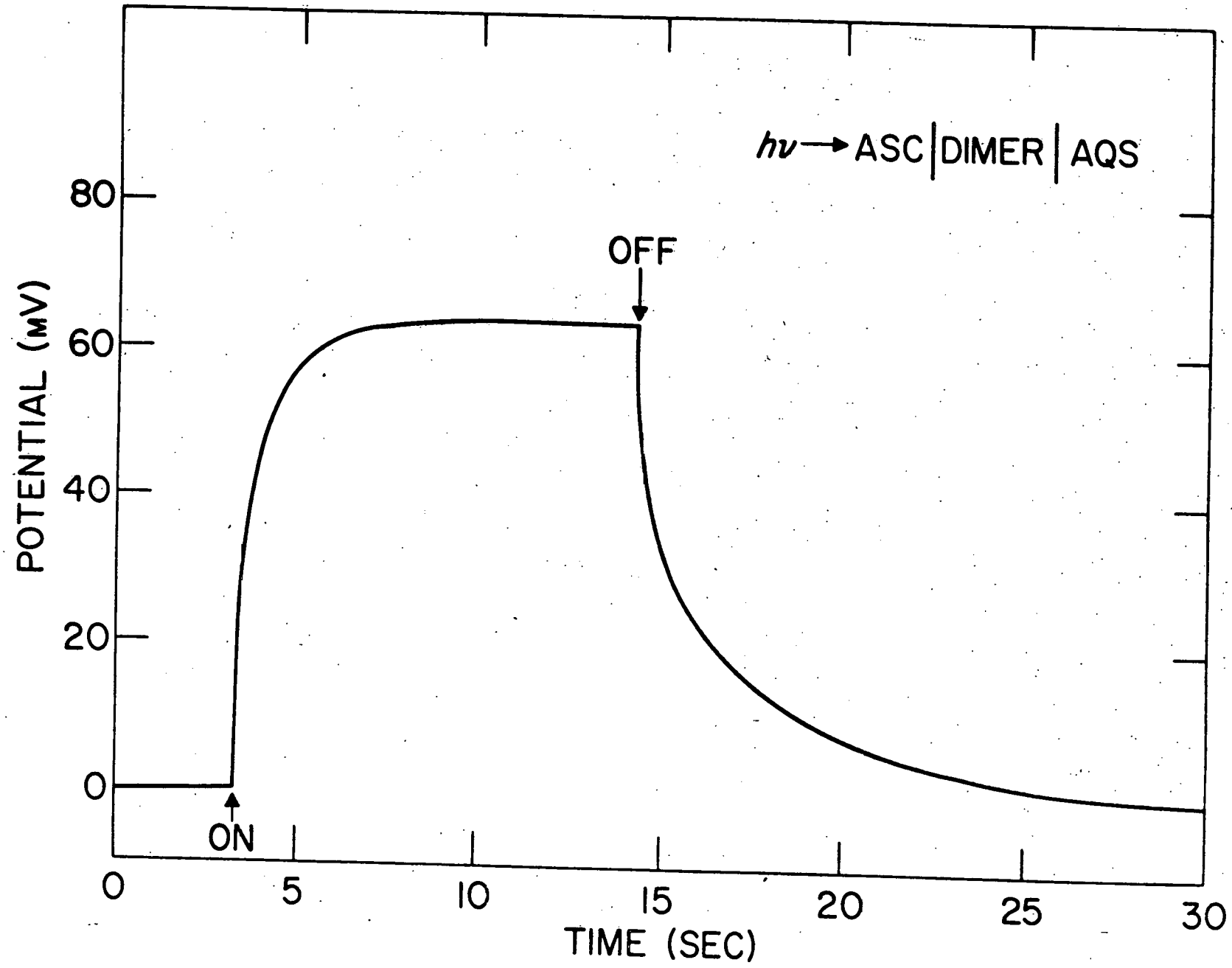

hν → ASC | DIMER | AQS
OFF
ON
POTENTIAL (mV)
80
60
40
20
0
0
5
10
15
20
25
30
TIME (SEC)

Figure 4