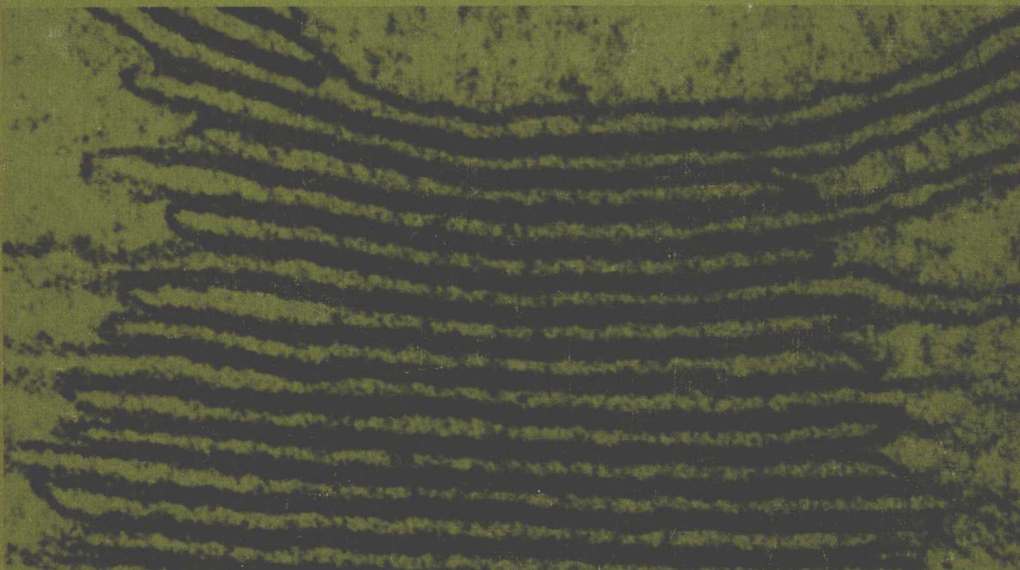
TOPICS IN PHOTOSYNTHESIS - VOLUME 3

PHOTOSYNTHESIS IN RELATION TO MODEL SYSTEMS

J. BARBER editor



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TOPICS IN PHOTOSYNTHESIS — VOLUME 3

Photosynthesis in Relation to Model Systems

edited by

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Foreword to Volume 3

This third volume in the series of Topics in Photosynthesis appears at a particularly appropriate time and with a particularly appropriate combination of subjects.

For some years now, there has been an increasing realization that alternative energy sources to the fossilized photosynthetic products of the recent past will have to be found; and the natural turn is to current photosynthetic systems for that purpose. While the actual green photosynthetic systems can and will be used as direct collectors and converters, they perhaps have a greater use as models for synthetic systems which might do more specific tasks. It is this particular relationship between our understanding of the photosynthetic process as such and the construction of model systems to accomplish one or another part of the total process to which this book is devoted. It reviews practically every approach that has grown up in the last decade or so toward this end. The construction of models to simulate photosynthesis, or some parts of it, has been going on for a long time. The purpose of this construction has been two-fold: one, to help understand the physical basis of the photosynthetic quantum conversion process and two, more recently, to possibly construct totally synthetic systems to achieve one or another of the objects of the photosynthetic process itself. It is in this latter role that the book will play its greater part. Anyone seeking to enter the field now will find this book a complete introduction to the various aspects of the subject that will allow him to make a choice most suited to his own interests and talents. There is hardly any doubt but that the use of our growing knowledge of the fundamental processes of photosynthesis will one day be the principal way in which our energy and materials sources will be achieved.

There still remains at least one approach to the natural process that has not yet been reported in the literature with any success. This is to simulate the two photosystems in two separate phases. One may expect this to happen in the very near future. Finally, the use of the separated charges, or stored energy, for the direct reduction of carbon dioxide to one-carbon reduced materials, has also yet to be reported.

Melvin Calvin

Preface

As with earlier volumes of this series the aim has been to produce a book centred around a specific theme. In this volume I have collected together a number of authoritative articles which high-light those aspects of the photosynthetic process which may have implications in the development of practical devices for solar energy capture and storage. Realizing that the book is likely to appeal to nonspecialists as well as to specialists, a deliberate effort has been made, where appropriate, to briefly explain the basic features of photosynthesis as well as cover the more specialized topics which are relevant to the theme of the volume. For this reason the book enables readers with various backgrounds and levels of training to appreciate the special features of the photosynthetic apparatus which would be worth consideration when trying to develop new technologies designed to help eleviate the energy supply problem which will inevitably arise as the reserves of fossil fuels diminish.

The first three chapters act as service chapters to the remaining portion of the book since they pin-point the basic energetic and structural features of the primary photosynthetic processes. In Chapter 1, Alexander Borisov covers some general aspects of the properties of solar radiation and goes on to emphasise the features of photosynthetic organisms which make them efficient solar energy converters. He has presented his arguments from the view of a physicist and emphasises the unique properties of the photosynthetic light harvesting antenna system and associated reaction centres which could form the basis for the construction of a photoelectric device. Chapter 2 is by Philip Thornber and myself and its purpose is to give a detailed description of how higher plants and other photosynthetic systems organise their pigments so that they can efficiently capture and transfer light energy to specialized reaction centres. It is explained how proteins help to keep the chromophores of the pigments at distances and orientations advantageous for energy transfer but avoid wasteful quenching processes. Chapter 3 is an excellent contribution by Robert Blankenship and William Parson. They discuss in detail various properties of photosynthetic reaction centres using the bacterial system as a specific example. This chapter covers the thermodynamics of charge separation and emphasises the ability of the system to resist back reactions. In Chapter 4, Professor Tien reviews mainly his own work using planar black lipid membranes and liposomes which have been made light sensitive by the incorporation of chlorophyll complexes extracted from chloroplasts. The next chapter, Chapter 5, is by V.P. Skulachev who describes experiments conducted by his group in Moscow in which photosynthetic bacterial chromatophores and reaction centres have been incorporated into artificial phospholipid membranes. Chapter 6 also deals with the making of artificial membrane systems which are light sensitive and able to produce photoelectric potentials. However in this case the pigment considered is bacteriorhodopsin and Thomas Schreckenbach has given a thorough review of both the properties and potential of this unique pigment-protein complex.

Although there is a great deal of interest in the possibility of using artificial membranes incorporating various light sensitive complexes, there is also the other alternative of stabilizing natural pigmented membranes against ageing. In Chapter 7, George Papageorgiou has reviewed the chemical background and progress being made in attempts to preserve the energy conserving properties of isolated thylakoid membranes. The following chapter (Chapter 8) is by Tony Harriman and myself and deals with the photochemical splitting of water into its elemental constituents. The initial part of the chapter outlines what is known about photosynthetic water splitting while the remaining part thoroughly reviews efforts being made to mimic this process using artificial photochemical systems. Chapters 9—11 deal with light induced hydrogen production. In Chapter 9 Professor Krasnovsky has given a general survey mainly based on work from his own laboratory touching on both artificial and in vivo systems. Chapter 10 by Rao and Hall and Chapter 11 by Hallenbeck and Benemann give comprehensive reviews on H_2 production from isolated chloroplasts and algae respectively. All three chapters emphasise and speculate about possible developments which could lead to a practical arrangement capable of generating significant amounts of hydrogen gas from illuminated photosynthetic systems. The final chapter (Chapter 12) of the book by Losada and Guerrero gives an interesting account of energy flow in biological cells and also emphasises that light mediated nitrate reduction to ammonia by photosynthetic organisms is a useful energy conserving process which could give rise to a useable fuel.

My task of editing this book has been made easier not only by the high quality of the contributions but also by the encouragement and help of several colleagues. In particular I would like to thank Cara Cherrett and my wife, Lyn, for assisting me with many of the tedious jobs involved in producing a volume of this type. Finally I wish to thank Professor Melvin Calvin for writing the Foreward. Professor Calvin was awarded the Nobel Prize in 1961 for elucidating the biochemical pathway giving rise to photosynthetic carbon fixation. For many years he has argued that the future development of man may require the manipulation and mimicking of the photosynthetic processes in order to take more advantage of the solar radiation which falls on our planet; a concept which is the basis of this volume.

J. Barber

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Chapter 1

Photosynthesizing Organisms: converters of solar energy

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1.1. INTRODUCTION

The energy crisis on our planet is becoming more and more grave. In the near future only solar energy and energy derived from nuclear fusion will be able to meet the global energy requirements of mankind. Until now the main effort and expense has been directed towards the development of thermonuclear devices. Although great progress has been achieved in this field, the problem is still far from being solved. But is this choice justified? Or maybe we owe this success to the fact that for the last few decades enormous sums of money have been spent on studies of the atomic nucleus, particularly for military purposes? If we forget what has been done in this respect and compare the two directions, solar energetics will undoubtedly seem more promising. In fact, visible solar radiation, when absorbed, hardly ever causes destruction of substances and "softly" generates EMF of the order of 1 volt, whereas nuclear reactions yield substances in a plasmic state at immense temperatures, with energy quanta being equal to megavolts, which means explosions that have to be harnessed. Moreover the use of these thermonuclear devices is always fraught with the danger of radioactive contamination of environment.

But there is one more thing that should be considered. The Earth's surface receives $3 \cdot 10^{24}$ J of solar energy per year. The bulk of it is absorbed in the Earth's biosphere and heats it. The thermal balance of our planet is to a great extent determined by absorption of solar radiation. As a consequence the temperature of the Earth, averaged over all geographical regions within a year, is about 280° K. However for solar radiation, this temperature would only be determined by geothermal heat streams and by irradiation into cosmic space and would be lowered to a value of at least 250° K. The estimated consumption of energy by mankind must reach, by the years 2010—2020, $2 \cdot 10^{21}$ J per year, i.e. about a thousandth of the solar energy heating our planet. If all this energy was to be generated by thermonuclear devices, the average temperature of the Earth's surface may increase by $10^{-3} \times 250° = 0.25°$. Despite the insignificance of this increase compared to yearly temperature fluctuations in certain regions of the Earth, it exceeds fluctuations of the average yearly temperature all over the planet and such heating — if it lasted for a long time — might bring about significant changes in climate, geographical environment, living conditions of plants and animals etc. In fact, a great number of anomalies observed in the recent years in our surroundings (e.g. increase of the concentration of CO_2 in atmosphere and decrease in the level of ozone, pollution of land, air and water, dying water basins, extinction of many species of animals and plants, rapid growth of harmful bacteria adaptable to newly formed ecological niches and many other things) can be attributed to the fact that mankind has at his disposal powerful sources of energy. Had the 4 billion people inhabiting our planet led a "patriarchal" mode of life, they would have attained nothing of the sort by themselves. Moreover the population explosion in this century has been paralleled by a decrease in the rest of the animal biomass, so that the balance of the plant and animal kingdoms has on a whole been retained. It seems to be high time to establish an international organization (probably, under the auspicies of the United Nations Organisation) that would work out the tactics and strategy of the development and stabilization of the World's energy systems. Such an organisation should foster the people's efforts to search for the most rational ways of energy planning with the view to restraining the chaotic growth of the power capacities that are at present improvidently exploited by nations in their own interests to the overall detriment of the whole of mankind, not forgetting the needs of our grand-children and even our children.

The situation seems to be less tragic when we speak of solar energetics. The sun heats the Earth and utilization of part of this energy would hardly change the thermal balance of the planet. No CO_2 or other harmful carbon products would be evolved into atmosphere. Therefore, in my opinion, our future energy needs must to a great extent be satisfied by utilisation of solar radiation. It is possible that mankind's survival depends on whether this choice is made.

1.2. SOLAR RADIATION

Beyond the gas envelope of the Earth the intensity of solar radiation is about 1.3 kW · m^{-2}. Its spectrum (curve S(λ) Fig. 1.1) approximates to the irradiation of an absolutely black body at 5000—6000° K. Here the basic question arises about the "quality" of this kind of energy. The thermo-dynamic approach to this problem was undertaken by several authors for particular photochemical and photoelectric systems. In the work of

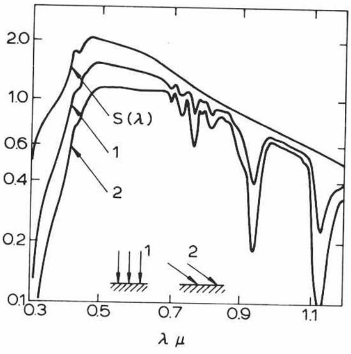

Fig. 1.1. The spectra of solar radiation. S(λ), in space; (1), attenuated after penetrating one air mass; (2), after penetrating two air masses.

Leontowitch (1974) the general thermodynamic approach to this problem was elaborated.

Taking into account the spectrum and the intensity of solar radiation, the high degree of parallelism of solar rays, the possibility of realization of non-reflecting absorbers etc. Leontowitch came to the conclusion that the thermodynamic yield of solar energy conversion could be as high as 93%; a value which is several times more than the level currently achieved. The situation is slightly worse at the Earth's surface. Even for normally falling rays (the inclination at 0°, curve 1) the radiation energy is weakened 1.5-fold due to light absorption and scattering by the atmosphere. Curve 2 in Fig. 1.1 represents attenuation of solar radiation inclined at 60° which means that the light path through the Earth's gas envelope is doubled. The cloudiness and pollution of air would also cause additional reduction of solar light reaching the Earth's surface. Furthermore, light scattering and refraction decrease the degree of parallelism of solar rays causing inadequate energy condensation. All this makes it difficult to obtain thermodynamic evaluation of solar energy conversion. But there is an easier way to solve the problem. It is known that physical solids can be heated up to ~3000°K if incident solar light is condensed by a parabolic mirror. Consequently, according to the basic law of thermodynamics:

$$\varphi_s = \frac{T_2 - T_1}{T_2} = \frac{3000^\circ - 300^\circ}{3000^\circ} = 0.90$$

Even if averaged over the daytime in accordance with the radiation intensity, the mean value of φ_s will be not less than 0.80—0.85 for the middle latitudes.

Consequently, we must conclude that solar radiation is energy of rather high quality. Batteries incorporating fine inorganic crysals are already used for conversion of solar into electrical energy, mainly in space vehicles, and the maximum realized energy conversion is as high as 20%. Several other projects for solar energy utilization are now being developed very intensively especially those involving geliothermal systems providing electricity, semiconductor photoelectric systems based on silicon and some other materials, and also some minor ones using wind, ocean waves, temperature gradients in oceans etc.

But the ultimate solution of the energy problem should also include its transport over large distances (thousands of kilometres) and storage. Therefore a search for new ways of utilizing solar radiation, especially involving, electrical energy generation (to which our present day technology is mostly adapted) or photocleavage of water and subsequent utilization of hydrogen, are of great importance.

In my opinion, the solution of these problems may be facilitated by unraveling the molecular mechanisms of the primary processes of photosynthesis in which the above two goals are to a certain degree coped with.

1.2.1. Accumulation of solar radiation by world photosynthesis

The total amount of solar energy falling yearly on the perimeter of our planet is immense—$3 \cdot 10^{24}$ J. About 60% of it is absorbed by the biosphere of the Earth, the rest diffuses in cosmic space. World photosynthesis conserves in biomass about $3 \cdot 10^{21}$ J per year, i.e. the efficiency is ~0.1%. Many cultivated plants conserve from 0.2 to 0.3% of the light falling on their leaves. Under optimal conditions (carefully arranged inter-row distances, watering and fertilization, temperature control etc.) agricultural crops may reach an efficiency of 1%, while for optimal organisms, like the alga *Chlorella*, or in some tropical plants, like sugar cane, the efficiency can reach 2—3% (see the works of Hall (1976), Calvin (1976) for more details). These figures show that improvements of all agricultural systems and even cardinal reorganization of the present-day rural economy, should be considered carefully. It also seems that biomass production from large scale algal culturing could become important as an economic chemical processing fodder etc. in the near future. Thus all agricultural, physiological, biochemical and genetic efforts resulting in an increase of photosynthesis production (food, fiber, dyes, medicines etc.) are of the greatest importance. But in photosynthesis Nature has also created an original photoelectric system which is coupled to a very complicated set of subsequent biochemical processes. Below arguments are given to show that the efficiency of solar energy conversion by this system is considerably greater than would be imagined at first sight.

1.2.2. Photoelectric systems

Let us consider the branch of solar energetics associated with the conversion of light into various forms of electrical energy. The following formula for efficiency of solar energy utilization will fit all the systems of this type:

$$\varphi_s = \frac{\int^{\lambda_m} S(\lambda) \cdot \overline{T(\lambda)} \cdot A(\lambda) \cdot \varphi_e(\lambda) \cdot \lambda/\lambda_m [1 - \Delta W_s (hc)^{-1} \lambda_m]\, d\lambda}{\int^{\infty} S(\lambda) \cdot \overline{T(\lambda)}\, d\lambda} \tag{1}$$

$S(\lambda)$ is the spectrum of solar radiation in space (curve 1, Fig. 1.1), $\overline{T(\lambda)}$ is the atmospheric transmittance in a given region averaged over a year; $A(\lambda)$ is the absorption of the system; λ_m is maximal wavelength of the quanta used by the system; λ/λ_m is the "devaluation" coefficient for shorter wavelength quanta; $\varphi_e(\lambda)$ is the spectral dependence of the quantum yield of photocurrent generation; ΔW_s is the portion of energy losses in the course of stabilization of new energy carriers (the pairs of charges of opposite signs); $hc \cdot (\lambda_m)^{-1}$ is the energy of long wavelength quantum.

Clearly $\int S(\lambda) \cdot \overline{T(\lambda)} d\lambda$ represents incident solar energy for systems located at the Earth's surface. Southern deserts with maximal numbers of sunny days and low air pollution provide mean yearly insolation exceeding 150 $w \cdot m^{-2}$ which are obviously most attractive for such systems.

Based on economic calculations, the minimal value of φ_s for conventional photoelectrical systems should exceed 6—8%. Out of many photoelectric systems known (for example, photovoltaic cells, photochemical redox reactions, artificial membranes adsorbing some subcellular particles or incorporating dye molecules, photoelectrochemical cells etc.), only present day semiconductor photocells based on superpure inorganic crystals meet this requirement. It should be noted that all the above mentioned systems are not very much different in λ/λ_m; $A(\lambda)$ and $[1-\Delta W_s(hc)^{-1}\lambda_m]$ factors. Consequently, factor $\varphi_e(\lambda)$ plays a decisive role in formation of their φ_s values. All other systems have $\varphi_e < 10\%$ and, respectively φ_s not exceeding several per cents.

Below it will be proved that one more efficient photoelectric system exists which has its φ_e close to unity and $\varphi_s \cong 10\%$ i.e. having values quite acceptable for conventional photoenergetic systems. This is the photoelectric apparatus of photosynthesis.

The above statement does not contradict the information given in Section 1.2.1 about photosynthetic organisms. It simply means that the portion of converted solar energy is considerably higher at the primary stages of photosynthesis than at the later stages.

Below the φ_s value is estimated for photosynthesis.

1.2.3. Energetics of the primary stages of photosynthesis

(a) $A(\lambda)$ Chlorophylls, like other dyes, exhibit rather narrow resonance-type absorption bands with halfwidth equal to several hundreds of cm^{-1}. However, due to several optical tricks invented by Nature in the course of evolution, the portion of solar radiation absorbed by plants reached 35—40%. These optical achievements are: (i) the diversity of spectral forms of chlorophyll (for example two basic pigments of plants Chl *a* and Chl *b* exist in vivo in more than ten forms with their absorption peaks dispersed in the region of 665—730 nm); (ii) specifically arranged surfaces of leaves decreasing the portion of reflected light; (iii) the specific characteristics of leaf cover operating as a trap of solar light even in the yellow-green optical region.

(b) λ/λ_m This factor diminishes φ_s especially in blue-green optical region because for plants λ_m = 700 nm (and correspondingly 840 and 870—890 nm for green and the most of purple bacteria). Fortunately, the portion of incident quanta is not very abundant there.

(c) ΔW_s The redox potential for oxidation of reaction centres is known to be +(0.45—0.50) volts (see, for example Kok et al., 1964). It was demonstrated in the work by Kok et al. (1965) that photosystem I is capable of photoreducing several viologen dyes with middle potentials reaching —0.60 V. Consequently, we may conclude that approximately one electron-volt of energy can be stored at the primary photoelectric stages from each quantum of electronic excitation entering the reaction center (i.e. λ_m = 700 nm and hc. $(\lambda_m)^{-1}$ = 1.75 eV).

Taking into account all above figures and using conditionally $\varphi_e = 1$ for the longest wavelength (λ_m) we arrive at the important conclusion: at the photoelectric stages of photosynthesis (i.e. separated charges of opposite signs stabilized in the millisecond time region and available for subsequent diffusion limited reactions) the portion of converted solar energy (in the form of electrical dipole) may be as high as 13—18%.

The next section will be devoted to estimation of φ_e values in the actual photosynthetic apparatus.

1.3. DELIVERY OF PHOTOINDUCED EXCITATIONS FROM ANTENNA MOLECULES TO REACTION CENTRES IN PHOTOSYNTHESIS

1.3.1. Quantum yield

There have been many studies to determine the quantum yields of photosynthetic primary charge stabilization. Usually they have been measured by following the photooxidation of reaction centres or cytochromes which are tightly coupled with them.

The most precise measurements were performed with preparations of the reaction centres (RC) isolated from carotenoidless mutant *Rh. sphaeroides* R-26. According to the data (Wraight, Clayton, 1974), in these particles, which are completely devoid of antennae pigments, $\varphi_e = 1.02 \pm 0.04$, i.e. is almost equal to unity.

In other particles which have been investigated (chromatophores, chloroplasts and their subunits), and also with intact cells, light is primarily absorbed by the antenna pigments and in these cases φ_e is found normally to be less than unity. This is because the determination of the φ_e value is subject to much greater errors, due to uncertainties in optical measurements associated with light scattering. Besides, in any experimental suspension there are always dying cells with decaying pigment and young ones with an underdeveloped antenna and RC. In normal cells, especially in subcellular particles isolated from them, there can exist defective chlorophyll domains, or some of the RCs may be in an inactive state. Hence considerable divergence in the results can be obtained in different laboratories even when using identical preparations from the same organisms. However numerous data give φ_e in the range from 20 to 80% (see, e.g. Clayton, 1962; Vredenberg and Duysens, 1965; Vredenberg, and Slooten, 1967; Sybesma and Beugeling, 1967). The main difference between all these various experimental systems and RC particles is that the former have a well developed molecular antenna. It is known that in the majority of purple bacteria there are on the average 30—200 antenna chlorophyll molecules per RC (plus almost the same amount of carotenoid molecules); in algae and higher plants this ratio is 150—400 : 1, and in green bacteria it is even up to 1,000—1,500 : 1 according to Olson et al., (1976).

Thus our major conclusion is the following: *the value of the quantum yield for the primary separation of opposite charges in photosynthesis (generation of microcurrent in the photosynthetic electron transport chain) is determined by the processes of energy transfer from light-harvesting antenna to reaction centres.*

But for our purpose, which is to reveal the maximum possibilities of photosynthesis as expressed by a high value of φ_s, the optimal $\varphi_e(\varphi_e^{max})$ values obtained in well organized, fully active chlorophyll domains, rather than its mean values, are of importance. To find them, Barsky and Borisov (1971), Borisov and Il'ina (1973), Barsky et al. (1974), have developed an original method using only relative measurements. They succeeded in determining φ_e^{max} with an accuracy of not less than ±(5—10%) *).

The idea of the method may be presented as follows. Let us designate the concentrations of active and inactive RC as $[P_a]$ and $[P_i]$, respectively. Then the major assumption is that the rate (V_{ph}) of useful trapping of singlet electronic excitations induced by light in the antenna is proportional to the portion of active RC:

$$V_{ph} = K_{ph} \cdot \frac{[P_a]}{[Pa] + [Pi]} = K_{ph}(1 - x) \tag{2}$$

where $x = P_i/[P_a] + [P_i]$ is the proportion of inactive RC.

Numerical example. Supposing at $x = 0$ (all RC are active) the rate of photosynthesis is 9 times as high as the total rate of useless losses of electronic excitations (V_Σ);

$$V_{ph}^{max} = V_{ph}(x = 0) = K_{ph} = 9V_\Sigma$$

Then the φ_e^{max} will apparently be

$$\varphi_e^{max} = \varphi_e(x = 0) = \frac{V_{ph}^{max}}{V_{ph}^{max} + V_\Sigma} = 0.9$$

* The specificity of the method is well illustrated by the following example. Supposing we have a suspension of cells or particles in which half of the antenna chlorophyll is not active ($\varphi_e' = 0$), and the second half has $\varphi_e'' = 0.9$. Then the classical method of determining φ_e by the ratio of moles $P + h\nu \rightarrow P^+$ to moles of chlorophyll-absorbed quanta of light will evidently give φ_e (average) = 0.45. Our relative method in this case will again give $\varphi_e^{max} = 0.9$, so we shall still be uncertain whether a fraction of inactive chlorophyll exists.