ON THE PROPOSED ENERGY SWITCH IN PHOTOSYNTHESIS

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ABSTRACT This paper analyzes the "energy switch" that has often been proposed to direct quanta absorbed by a given photosynthetic unit alternately to the site of one and then the other primary reaction. Such a device is essential to the Franck-Rosenberg theory, but not to the Duysens-Witt-Kok (DWK) model, which needs to assume only that the reactions occur in series. If there is no energy switch, an incident quantum absorbed at any time by any particular pigment molecule stands a chance of ending up in the reactive site of either primary reaction. The "separate packages" model is a special case of this general picture. Without an energy switch, a series model requires a storage device to insure that a quantum will not be wasted if it arrives at the site of one reaction while the photosynthetic unit is set up to perform the other. Such a storage device can be appended to the DWK model. Alternatively, this model can be augmented by an energy switch. This gives what is commonly known as the "spillover model," a confusing name which we suggest be abandoned. As a clear-cut–though perhaps technically unfeasible–test of the energy switch hypothesis, we imagine a quantum injector, a hypothetical source of flashing light which delivers a single quantum to every photosynthetic unit with each flash. We aim this useful figment at an (equally hypothetical) photosynthetic system all of whose units are set up to perform the same primary reaction. If there is an energy switch, we can now prepare a "synchronous" photosynthetic apparatus in which each photosynthetic unit is undergoing the same reaction at the same time.

The wealth of information provided by the experiments of Kok (Kok and Hoch, 1961), Witt (Witt, Müller, and Rumberg, 1963), Duysens (1964), and many others has made it probable that the two primary reactions of photosynthesis operate in series rather than in parallel. Two sets of reactions, one of which operates on a ground state product of the other, alternate in a two stroke cycle that transfers one electron from water to a primary oxidant, perhaps ferredoxim (Clayton, 1965 *a* and *b*). This series model carries with it the implication that somewhere in the photosynthetic unit there is an alternating mechanism that is by turn "set up" for products of the first and the second reaction. This may, for example, be a molecule that is oxidized by the first reaction and reduced by the second.

The purpose of this paper is to analyze whether incoming quanta are trapped in series or in parallel. In other words, does a photosynthetic unit direct quanta alternately to the active site of one and then the other primary reaction? If such an arrangement is present in each unit (with possible exceptions for units occupied in dark "setting up" reactions or engaged in a waste process because of some inhibition), we shall say that there is a "energy switch." (The phrase is Clayton's (1963*b*); the idea is originally due to Franck (1958).)

If there is no energy switch, a quantum absorbed at any time could end up in the reactive site of either primary photochemical reaction. (By primary reaction we mean a chemical reaction in which an excited state of a molecule takes part; that molecule we call the active site of the reaction on the assumption that it is a permanent part of the structure of the photosynthetic unit.) Except for saturation effects, the relative probability that a given quantum will land in one or the other site depends only on the chemical identity and geometric position of its absorber, not on the fate of the last quantum absorbed by that unit. In the most usual formulation of the no-energy-switch model, there are two "separate packages" of pigment molecules, each of which funnels energy to one and only one of the two primary reactions. This assumption is more restrictive than necessary. We may instead suppose that many or even all of the pigment molecules are in a "borderline" region and stand some chance of feeding a quantum to either reaction.

The series hypothesis imposes a considerable constraint on a model without an energy switch. Suppose, for example, that the chemical apparatus of a particular photosynthetic unit has just completed reaction 1, and that the next quantum absorbed by that unit again finds its way to the site of reaction 1. If there is no energy switch and such a quantum were wasted, the photosynthetic unit would in general be wasting half the photons incident upon it.

We must instead assume that the energy from such a photon will somehow be stored until it can be used. This stored energy might take the form of a chemical species designed specially for the purpose, a trapped exciton or electron in the bulk pigment or at the reactive site, or an intermediate in the normal sequence following the first primary reaction. If the quantum is stored as a chemical intermediate, it follows that each of the two primary reactions takes place whenever a quantum becomes available—in parallel, so to speak. A later dark reaction operates alternately on products of the first and the second reaction, and in so doing provides the series character. We could, of course, have our misdirected quantum continue on to the second reactive site of this or some other unit where it is needed–but this would be precisely the energy switch we began by excluding.

This paper specifically does not consider purely parallel models like that of Arnold (1965) or those reviewed by Clayton (1963*a*).

Spillover and the Energy Switch. In general, the "flip-flop" mechanism required for an energy switch could be designed in one of three ways: (*a*) There is one active site for the two reactions, a molecule or small group of molecules that is by turn set up to perform the first and then the second primary reaction. (*b*) There are two separate sites for the two reactions. Each primary reaction so changes the energy transfer pathways or trapping properties of the photosynthetic unit that the next quantum incident on that unit goes to the other site. In other words, each primary reaction "sets the switch" for the other. (*c*) There are again two separate reaction sites. The switch for the second reaction is set, not by the first primary reaction itself, but by a chemical intermediate one or more steps down from the first primary reaction. A similar situation might obtain for the resetting of the first switch.

The details of the trapping and switching processes are not important for the present analysis. It is simplest for our purposes to think of the two switches as deep traps, each of which feeds energy to one of the two primary reactions and disappears after it has done so. Trapping may be by means of a "long wavelength pigment;" i.e., radiationless decay into some singlet state of energy lower than that of the lowest excited state of the bulk pigment. It might be a singlet-triplet crossover, perhaps enhanced by a nearby heavy atom, followed by radiationless decay into the lowest triplet of the trap molecule. It might even be some change in excited state geometry (e.g. excimer formation) that slows energy transfer to adjoining pigment molecules. A fourth possibility is that the trapping and the photochemistry are the same; i.e., that excitation would migrate away from the active site the photochemically active molecule not immediately attacked by its "substrate."

In order for a model with an energy switch to explain the Emerson effect (Emerson and Rabinowitch, 1960), it must suppose that there are two kinds of pigment molecules, an *ef*ficient set (system II) that can supply quanta to one site or the other as needed, and a *de*ficient set (system I) that can supply quanta efficiently to one site but not to the other. If there is an energy switch, photosynthesis will be fully efficient under light absorbed only by system II; if there is none, photosynthesis will be fully efficient only under conditions of Emerson enhancement, or under monochromatic light of a particular wavelength at which the two systems are in balance (Myers and Graham, 1963).

The energy switch must insure that quanta absorbed by the deficient system I are not wasted during Emerson enhancement. When both systems are absorbing light simultaneously, *ef*ficient pigments must be more likely to feed reaction 2, *de*ficient pigments reaction 1. A quantum absorbed by the *ef*ficient system II of a given photosynthetic unit must therefore know whether any units nearby are set up for reaction 2. Before this quantum can be used to feed reaction 1, it must visit the reaction sites of several units (and perhaps their bulk pigments as well) looking for a unit set up for reaction 2.

This is the basis for the suggestion by Franck and Rosenberg (1964) that quanta migrate through a "superunit" before they are trapped and used for photochemistry. This hypothesis is similar to the older idea that the photosynthetic unit is not a well-defined structure but is simply a division of labor between energy catching and photochemically reactive chlorophyll *a* in an otherwise more or less continuous pigment array. Still, it does not necessarily conflict with the identification of the photosynthetic unit with the quantasomes studied by Park and coworkers (1964).

Previous discussions of possible models for the primary processes of photosynthesis have focused on the choice between spillover and "separate packages." We feel that it would be simpler and more fundamental to ask whether or not there is an energy switch. We have already seen that the separate package model is a special case of the no-energy-switch picture in which pigment molecules are partitioned into nonoverlapping packets, each of which feeds energy exclusively to one or the other primary reaction. More generally, system II may include borderline molecules which may feed either reaction, depending on the random journey of a particular quantum. Quanta absorbed by these molecules are likely to pass through system I (i.e. those molecules which can feed only the first reaction) on their way to the first reactive site. This would give the appearance of spillover from system II to system I despite the absence of an energy switch. We therefore suggest that the term spillover model be abandoned, and that spillover be used to refer to energy transfer from system II to system I in any model.

In summary, there are three general "black box" (or, more appropriately, "green box") models for energy transfer between the pigment systems of the photosynthetic unit: (*a*) energy switch; (*b*) no energy switch, with separate packages; (*c*) no energy switch, with a borderline region within range of both reaction sites. It will not be easy to rule out any of these possibilities. Suppose, for example, that a fractionation procedure were discovered that made it possible to isolate system I and system II as separate particles, a possibility suggested by the experiments of Boardman and Anderson (1964). To establish model (*b*) it would still be necessary to prove that no energy transfer takes place between these particles in vivo, or at least that such energy transfer was not essential to efficient photosynthesis. Probably the easiest way to do this would be to show that light absorbed exclusively by system II was unable to feed some purely system I reaction.

EXPLICIT MODELS

The Duysens-Witt-Kok (DWK) Model. Probably the most widely used of the explicit models now in the literature was developed by Duysens (1964), Witt et al. (1963), and Kok and Hoch (1961), from their independent but complementary studies of changes in the absorption and emission spectra of photosynthesizing systems. The first reaction in this model consists of the reduction of a primary oxidant and the oxidation of a special form of chlorophyll *a* (P700). This now oxidizes a cytochrome that in one or more steps oxidizes a molecule of Q, believed to be a quinone. Q has special fluorescence quenching properties that will be discussed later. The second reaction re-reduces Q and produces an oxidizing agent that oxidizes water to O_2.

The authors of the Duysens-Witt-Kok (DWK) model started from observations of spectroscopic changes induced with light of one wavelength and reversed with light of another. These were explained most simply by a series model (Clayton, 1963*a*, 1965 *a* and *b*). The second reaction acts directly on Q, which is (by way of several intermediates) a ground state product of the first. We have already pointed out that such a model requires one of two devices to insure efficiency: either the assurance that quanta will be delivered alternately to each reaction site, or else some provision for storing quanta which reach the site of one reaction when the photosynthetic unit is set up for the other.

As originally presented by Duysens (Duysens, Amesz, and Kamp, 1961), the DWK model assumes the separate package model and hence no energy switch. We have already pointed out that this picture may be extended to include borderline pigment molecules with a fixed probability of feeding either reaction. It can be further adapted to our new requirement of a storage device if we add the assumption that the large number of intermediates between P700 and the long-lived Q makes it possible for several quanta to be absorbed by package 1 and stored as oxidized P700 or oxidized cytochrome even when the unit is "set up" for reaction 2 (i.e. even when Q is in its oxidized form). We might expect to see direct experimental evidence of this quantum storage. The first part of the electron transport system would then have a "capacity for more than one electron" (Bannister and Vrooman, 1964).[1]

The Franck-Rosenberg Model. The second most prominent model for the primary processes of photosynthesis, that proposed by Franck and Rosenberg (1964), begins with the fact that the fluorescence quantum yield from actively photosynthesizing cells is half that from cells that have been "emptied of photosynthetic reactants," for example by prolonged irradiation in the absence of CO_2. (The fluorescence referred to is the one with maximum emission at about 680 mμ.) This observation led Franck and Rosenberg to posit that (*a*) the two primary reactions not only act in series but also require quanta delivered in alternation by means of an energy switch; (*b*) at least one primary reaction must involve an excited singlet state, since otherwise fluorescence would be unchanged by the presence or absence of photochemistry; (*c*) the entire yield of fluorescence emission during normal, maximally efficient photosynthesis (exclusive of "long wavelength fluorescence," which they considered separately) is a by-product of one and only one of the two

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[1] *Note Added in Proof.* Joliot (1965) has presented kinetic evidence for such a quantum storage device in the form of a pool of intermediates between system I and system II.

primary reactions; (*d*) fluorescence is emitted solely by the active site of that reaction (the first) with none at all coming from the bulk pigment, since otherwise there would be a constant emission from the bulk pigment regardless of which reaction was being fed; (*e*) the first reaction proceeds by way of a metastable state of the active site molecule, the transition to which is slow enough to allow a 6% quantum yield of fluorescence from the active sites of those units that are set up for the first reaction; (*f*) back transfer of excitation from the trap to the bulk pigment is slow enough to allow time for fluorescence to take place from the trap alone.

These six basic conclusions led Franck and Rosenberg to a self-consistent model radically different from those provisionally held by most other workers in the field. In this model, there is only one active site for the two reactions. The second primary reaction is the attack of an "adsorbed" (complexed) reactant on the lowest excited singlet state of the active site. The first reaction is between a diffusible substrate and a metastable triplet state of the trapping molecule. The triplet is subject to waste photooxidations which are responsible for the effects observed when photosynthesis is carried out under system I light.

More recent work (Arnold and Davidson, 1963; Arnold, 1965) has raised the possibility that in vivo fluorescence may be due to a more complicated process than the one discussed by Franck and Rosenberg. At the same time, Hoch (1964) and Hoch and Owens (1963) have cast some doubt on the currently accepted series model by demonstrating a more complicated relationship between photosynthetic and respiratory oxygen than had previously been supposed. Until these questions can be settled experimentally, it is worth asking whether the DWK model can be adapted to provide alternating delivery of quanta to each of the two reaction sites, and thus to satisfy at least some of the requirements laid down by Franck and Rosenberg. This leads us to the so-called spillover model, a name we have criticized in a previous section.

The "Augmented DWK Model." The outlines of a DWK model augmented with an energy switch have been offered many times (Clayton, 1963*b;* Hoch, 1964; Kok, 1963; Myers, 1963). The first reaction produces an intermediate which is complexed with a chlorophyll *a* molecule at the site of the second reaction. This "sets" the trap for the second primary reaction. An efficient quantum absorbed by a given photosynthetic unit first visits the second reaction site of that unit. It is trapped there if the complexed reactant attacks the excited singlet state of the site chlorophyll *a* before the excitation can migrate to a neighboring molecule. Let us suppose that this does not happen. If there is a superunit, the quantum "checks out" the second reactive sites of several more units and is trapped if any of them is set up to receive a quantum. Any quantum that survives this journey passes on to the first reactive site of some unit and is used for the first reaction.

This augmented DWK model satisfies the requirement laid down by Franck and Rosenberg that at least one of the primary reactions proceeds by way of an excited singlet state of chlorophyll *a*. It also explains the increase in fluorescence yield when the photosynthetic apparatus is "emptied of reactants," since under these conditions there are no complexed reactants to trap a migrating exciton. Unlike the Franck-Rosenberg model, it does not require that the first reaction proceed by way of a metastable state.

According to both versions of the DWK theory, in vivo fluorescence comes from the bulk chlorophyll *a* and is quenched whenever the agent *Q* is in its oxidized form. At first sight, one wonders how the oxidized or reduced state of a single molecule can affect the fluorescence emitted by a large aggregate without wasting large amounts of energy as heat. This difficulty disappears if we suppose that *Q* is the energy switch and traps a quantum looking for a unit set up for reaction 2 simply by reacting with a molecule that the quantum has excited. This is essentially the proposal of Franck and Rosenberg that *Q* represents not so much a quenching molecule as a quenching reaction.

The concept of a superunit requires that any quantum not trapped by the second reaction site of the unit in which it was absorbed must proceed to the second sites of several other units without falling into any of their first traps. This could be accomplished in one of two ways. We might suppose that the path of a system II quantum does not bring it within range of a first trap until it has toured several photosynthetic units. Alternatively, and contrary to popular opinion, the shallow "long wavelength trap" may actually be relatively inefficient because of a relatively low probability of excitation transfer from an adjacent chlorophyll *a* molecule or because of a relatively high probability of "back transfer" (Robinson, 1964). In either case, a quantum not trapped at the second reactive site of the unit in which it is first absorbed would have ample time to visit the sites of several other units before it finally fell into a trap leading to the first reaction. In vivo fluorescence in the augmented DWK model is a by-product of this extended migration, and comes from the bulk pigment. In the Franck-Rosenberg model, in vivo fluorescence at intensities well below saturation comes only from the trap, and then only as the by-product of one of the two primary reactions.

This disagreement makes possible a clear-cut test between the two models. In the Franck-Rosenberg picture, we should expect that from compensation up until those high intensities under which waste processes disrupt energy transfer within the photosynthetic unit and induce extra emission from the bulk pigment, the fluorescence emitted in response to the excitation of system II chlorophyll *a* should decay in a simple exponential curve whose lifetime is independent of light intensity and photosynthetic yield. This means that fluorescence lifetime should be independent of fluorescence and photosynthetic yield up to but not including intensities approaching saturation. In the augmented DWK model, on the other hand, fluorescence lifetime would depend on both the intensity and the spectrum of the incident light.

Just after this manuscript was submitted for publication, the author was informed that the experiment described above has been performed by A. Müller and R. Lumry at the University of Minnesota. The fluorescence lifetime in photosynthesizing whole cells of *Chlorella* turns out to be proportional to the rate of oxygen production from very low to saturating light intensities. It has not yet been firmly established that fluorescence yield is proportional to the rate of oxygen production in these organisms. Fluorescence yield, fluorescence lifetime, and rate of oxygen production are known to be linearly related in the Hill reaction of fragments of green plants, and it may turn out that this relation will also hold for *Chlorella* photosynthesis (Lumry, Mayne, and Spikes, 1959). If so, these findings would be a strong blow against the Franck-Rosenberg theory. Müller and Lumry interpret these and other data by means of an energy switch model rather different from the one outlined here.

The dependence of fluorescence lifetime on intensity and wavelength predicted by the augmented DWK model should be derivable by random walk calculations like those performed by Pearlstein (1964) on the separate package model. Such calculations should also show whether the model proposed here can be made to reproduce the observed difference between fluorescence lifetimes measured by the phase shift method and those measured by direct observation. This difference appears whenever the fluorescence decay curve is not a simple exponential.

The remaining differences between the DWK and Franck-Rosenberg models stem from two main issues. First, Franck and Rosenberg assert that there is only one active site for both reactions; DWK, that each reaction has a separate site. If there is no energy switch, separate sites are assured; otherwise, more direct experiments will be needed to settle this issue. Second, the two models offer different interpretations of some of the observations made on photosynthesizing systems exposed to system I light. To Duysens, Witt, and Kok, these observations reveal important events in the mainstream of photosynthesis; to Franck and Rosenberg, they are evidence for the diversion of quanta absorbed by the deficient pigment system I into waste photooxidations of chlorophyll *a* that throw the photosynthetic unit out of commission until they are reversed.

The Single Quantum Injector–A Thought Experiment. Most of the models for an energy switch now in the photosynthetic literature are presented the steady-state language natural to the working biophysicist. They consider an ensemble of photosynthetic units, some set up for the first and some for the second reaction, subject them to a steady light of a particular spectrum, and describe the over-all response of the system. This makes it possible to speak of spillover from system II to system I when reaction 1 is "predominant."

We may gain further insight by imagining that we had a source of flashing light capable of delivering to each photosynthetic unit with each flash one and only one quantum of the wavelength of our choice. We point this hypothetical machine towards an equally hypothetical photosynthetic system each of whose units has an energy switch set to direct the next incident quantum towards the first primary reaction. (We shall assume for the purpose of this discussion that this is the so-called long wavelength reaction.) A flash of *any wavelength* absorbed by the photosynthetic system from such a "single quantum injector" will now supply energy only to the first reaction, and make it possible to study that reaction all by itself. We should observe cytochrome oxidation (Duysens, Amesz, and Kamp, 1961), the bleaching of P700 (Kok and Hoch, 1961), a narrow ESR signal (Beinert, Kok, and Hoch, 1962), and all the other effects associated with system I. A second flash of quanta absorbed by system II would feed energy exclusively to the second primary reaction in each unit, a third flash (absorbed by either system) to the first, and so on. We would thus have made a preparation of photosynthetic units which are *reacting synchronously;* each unit would be performing the same primary reaction at the same time. In our idealized experiment, these flashes might be repeated indefinitely and the two reactions studied in isolation by differential absorption spectroscopy or by any other standard method.

Such a synchronous system would make possible a large number of interesting observations. It would first of all be possible to observe directly whether a given spectroscopic effect was associated with the first or the second reaction, or some more complicated interaction between the two. This would be a particularly useful approach to the study of light-induced free spins, which would probably be easily measurable after a single flash. The dark time needed to set up the switch delivering quanta to the second reaction could be determined by varying the interval between first and second flashes. As soon as the second flash comes too closely on the heels of the first, it would no longer produce the effects associated with "even" flashes applied at longer intervals. In effect, each unit would be receiving two photons from a single flash, and would show the manifestations of one of the processes to be discussed in that connection in the next section.

If it were in addition possible to measure the CO_2 absorbed and the O_2, reduced nucleotides and photophosphorylation produced by each individual flash, we might obtain direct information on how the energy from the transport of four electrons is combined to produce an oxygen molecule, as well as on the relationship of electron transport to the generation of ATP. With even more sophisticated instrumentation, we might be able to confirm directly the prediction of both Franck-Rosenberg and augmented DWK models that fluorescence comes either from the first reaction site itself or as a by-product of excitation seeking the first reaction site. The first, third, and all "odd" flashes should produce double the usual stationary-state yield of in vivo fluorescence with, however, the lifetime typical of actively photosynthesizing systems. The second, fourth, and subsequent even flashes of system II light should produce much less emission.

By using wavelengths absorbed by system I for even flashes, we could observe directly what happens when the deficient pigments try to feed quanta to the second reaction. This would provide direct information about the origin of the Emerson effect. A variant of this experiment would use a series of pairs of closely spaced flashes each separated by a relatively long time interval from the next pair. We should observe no difference between the photosynthetic quantum yield from two paired efficient flashes (i.e. flashes absorbed by efficient pigments) and that from a deficient followed by an efficient flash. Similarly, two paired deficient flashes would give much the same quantum yield as an efficient followed by a deficient flash.

What would be the response to our hypothetical experiment of a series model with a storage process but without an energy switch? Such a model would of necessity have a separate site for each primary reaction. If it were possible to aim our quantum injector at pigment system I or II at will, we could establish a synchronous system simply by injecting each odd quantum into system I, each even quantum into system II. We could then make observations entirely analogous to those described in the preceding paragraphs for the energy switch model. In addition, we could observe the quantum storage processes postulated earlier by injecting odd quanta into system II or even quanta into system I. In contrast to the energy switch model, we should get the same photosynthetic yield from the paired flash experiment whether the system I flash precedes or follows the system II flash, as long as the first quantum is still being stored at the time the second flash arrives. The pattern of spectroscopic or other direct observations should, however, depend on the order of the flashes. For that matter, all of the experiments described in this paragraph should work equally well in a parallel model with no series character at all.

Suppose, on the other hand, that our hypothetical machine could only deliver a quantum of a given wavelength to each unit, and that, once there, the quantum might be funneled to either system in proportion to its optical density at that wavelength. We should then expect that quanta from the first flash having the system II action spectrum will divide more or less evenly between those fed to the first reaction site and those stored for later use by the second. The results of both of these processes should be observable. Quanta from the second flash will be divided between the first and second reaction sites of units which had received either a "first" or a "second" quantum from the previous flash. At the end of two flashes, about half of the units will have gotten a quantum into both traps and will have achieved an electron transfer. The other half will have stored two first or two second quanta, and will be able to achieve an electron transfer only if enough of the "other" kind of quantum arrives before the stored energy decays into heat. There is also the possibility that one site will accumulate more quanta than it can store and be compelled to waste the excess. This argument can be continued for the third, fourth, and subsequent flashes.

Granted the series model, the hypothetical quantum injector proposed here provides a situation in which it would make a great deal of difference whether or not there is actually an energy switch. If therefore forces the proponents of any particular model to offer a clear and precise prediction of its response to a critical, even though hypothetical, experiment. It is now quite natural to ask the question: granted an energy switch, can synchrony be achieved experimentally?

Can Synchrony Be Achieved? The first requirement for an experimental synchronous system is a photosynthesizing preparation all of whose units are set up at the same time for the same reaction. On the face of it, there is nothing in the series model to distinguish a first from a second reaction; at the steady state each sets up the unit to perform the other. Fortunately, the experiments of French (1963) indicate that the long wavelength primary reaction is reversed by a dark process if it is not followed by the arrival of a second quantum within 5 to 10 sec. This reaction is thus first, and we have so called it throughout this paper. It would be very useful to know whether this dark reaction goes to completion; e.g., whether all photosynthetic cytochromes are in the reduced state in the dark. If it does, we should be able to prepare a photosynthetic system all of whose units are set up for the long wavelength reaction simply by keeping it in absolute darkness for ten seconds or so following a period of normal photosynthesis.

Serious difficulties still remain. Clearly, any flash intense enough to deliver at least one photon to each photosynthetic unit will deliver two or even more photons to many of them. A less intense flash, on the other hand, will miss many units entirely yet still deliver more than one quantum to each of many others. Our second requirement, then, is a source of flashing light so intense that it can deliver at least one quantum to every photosynthetic unit with every flash, yet with a lifetime short enough that a unit that absorbs two photons from a single flash will be unable to use more than one of them. There is no way of knowing in advance how short a lifetime this would require. First of all, the flash would have to decay faster than the time it takes to set the switch that directs the second quantum to the second reactive site. In the augmented DWK model, this is the time needed to generate Q and to convey it to the second reaction site; in the Franck-Rosenberg model, it is the time needed to complete the first (triplet) reaction, the intermediate Y being permanently complexed to the active site ready to attack as soon as the site is excited.

Beyond this, experimental preparation of a synchronously reacting system would depend on the response of a photosynthetic unit that has absorbed more than one photon from a particular flash. The extra quanta may be: (*a*) stored and used after the other reaction has taken place and the switch reset to its original position; (*b*) degraded harmlessly into heat; (*c*) diverted into waste processes that change the energy transfer properties of the unit or throw it out of commission; (*d*) passed around to other photosynthetic units that did not receive a quantum from that particular flash.

Of these possibilities the fourth is by far the best for synchrony. Flash energy might be distributed so efficiently within the superunit that flashes of roughly one quantum per photosynthetic unit per flash might suffice to establish synchrony. If all extra quanta are degraded harmlessly into heat (possibility *b*), we might achieve synchrony simply by applying flashes of such intensity that practically all units receive at least one quantum from each flash even though most of them receive more than one. There is likely, however, to be a limit to the number of quanta a unit can absorb from a single flash before it falls prey to the waste processes described in possibility (*c*). These would make synchrony a good deal more difficult. At flash intensities of one quantum per unit per flash, only a few units would receive exactly one quantum from each flash over a period of several flashes. The others would get out of step even if waste processes from units receiving two or more photons from some one flash did not interfere seriously. Higher intensities would insure that each unit received a quantum from each flash, but would greatly increase waste. Still, we might hope to find a flash intensity sufficient to insure that nearly all units receive at least one photon from each of several successive flashes, and in which the build-up of "burned-out" units could be distinguished experimentally from the main events of photosynthesis. Finally, it would be hard for our synchrony experiment to distinguish possibility (*a*) from the model with no energy switch. There is fortunately no reason to suppose that a plant would evolve a mechanism to store quanta from flashes of light much shorter and more intense than it would ever encounter in nature. Possibility (*a*) is therefore a very unlikely prospect.

In short, the flash lifetime needed for a synchronous system may be quite long–perhaps even longer than the microsecond lifetimes now commonly available. Alternatively, it may be as short as the lifetime of flashes from the *Q*-switched ruby laser (De Vault, 1964), or may be shorter than the lifetime of flashes presently available. A fourth possibility is that a flash may be found with lifetime shorter than the delay in setting up the trap for the second reaction, but that once that reaction has taken place, the unit is set up practically instantaneously to direct the next quantum to the site of the first reaction. In that case, we could maintain synchrony only for two flashes–but even this should make possible many interesting observations.

Finally, if the first reaction is in fact appreciably reversed in the dark, we might expect to obtain interesting information from any series system at all simply by observing the first flash after ten seconds or so of absolute darkness. This flash should produce observable changes different from those induced by subsequent flashes because it would find all photosynthetic units set up for the first primary reaction. Subsequent flashes would gradually establish a steady-state distribution of units whose photochemical apparatus is set up for the first or for the second reactions, plus units disabled reversibly or irreversibly by waste processes. This effect is not the same as the induction period, which is caused by the need for a gradual build-up of metabolic intermediates which are necessary for efficient photochemistry but which have been depleted during a minute or so of darkness.

CONCLUSIONS

This analysis of the energy switch, as defined by the *Gedankenexperimental* quantum injecting machine, is intended to make it easier to compare and contrast the radically different interpretations currently in use for the highly sophisticated and detailed data that continue to pour forth. Perhaps it is not too much to hope that the dream of synchronously reacting photosynthetic units will be realized in the laboratory. Even if this should turn out to be technically impossible, our hypothetical single quantum injector still has value as a bridge between model and experiment. Suppose that all difficulties were swept aside, and that it were actually possible to feed one quantum of light of a chosen wavelength into each photosynthetic unit at the same time. What experimental result would the model under consideration predict? If the answer to this question (or at least a number of distinguishable alternatives) is not plain, the model is not complete. Would the results calculated from a particular mathematical model be affected by the presence of an energy switch? If so, this additional possibility must be considered.

A curious language barrier has arisen between the proponents of rival models for the primary processes of photosynthesis, even though many of these were originally presented as little more than schematic diagrams. As an unfortunate byproduct of this confusion, chemical physicists seeking theoretical treatments of or in vitro analogues to photosynthetic processes have felt compelled to rely on one or another particular model in order to avoid an unpromising biological thicket. Much of this difficulty stems from the fact that these models often start from different sets of unstated assumptions about ultrastructure too small and energy transfer processes too fast for direct measurement. It may well turn out that some of these basic assumptions will change in the light of new experiments. Still, it is important to refine our present picture–if only so that we shall be able to tell when it is out of date.

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REFERENCES

ARNOLD, W., 1965, *J. Phys. Chem.*, **69**, 788.

ARNOLD, W., and DAVIDSON, J. B., 1963, *Nat. Acad. Sc.-Nat. Research Council Publ.* No. 1145, 698.

BANNISTER, T. T., and VROOMAN, M. J., 1964, *Plant Physiol.*, **39**, 622.

BEINERT, H., KOK, B., and HOCH, G., 1962, *Biochem. and Biophysic. Research Commun.*, **7,** 209.

BOARDMAN, N. K., and ANDERSON, J. M., 1964, *Nature,* **203,** 166.

CLAYTON, R. K., 1963*a, Ann. Rev. Plant Physiol.,* **14,** 159.

CLAYTON, R. K., 1963*b, J. Theoret. Biol.,* **5,** 497.

CLAYTON, R. K., 1965*a,* Molecular Physics in Photosynthesis, New York, Blaisdell Publishing Co.

CLAYTON, R. K., 1965*b, Science,* **149,** 1346.

DEVAULT, D., 1964, *in* Rapid Mixing and Sampling Techniques in Biochemistry, New York, Academic Press, 165.

DUYSENS, L. N. M., 1964, *Progr. Biophysics and Biophysic. Chem.,* **14,** 1.

DUYSENS, L. N. M., AMESZ, J., and KAMP, B. M., 1961, *Nature,* **190,** 510.

EMERSON, R., and RABINOWITCH, E., 1960, *Plant Physiol.,* **35,** 477.

FRANCK, J., 1958, *Proc. Nat. Acad. Sc.,* **44,** 941.

FRANCK, J., and ROSENBERG, J. L., 1964, *J. Theoret. Biol.,* **7,** 276.

FRENCH, C. S., 1963, *Nat. Acad. Sc.-Nat. Research Council Publ.* No. 1145, 335.

HOCH, G., 1964, *Rec. Chem. Progr.,* **25,** 165.

HOCH, G., and OWENS, O. v. H., 1963, *Nat. Acad. Sc.-Nat. Research Council Publ.* No. 1145, 409.

JOLIOT, P., 1965, *Biochim. et Biophysica. Acta,* **102,** 116.

KOK, B., 1963, *Nat. Acad. Sc.-Nat. Research Council Publ.* No. 1145, 301.

KOK, B., and HOCH, G., 1961, *in* Light and Life, Baltimore, Johns Hopkins Press, 397.

LUMRY, R., MAYNE, B., and SPIKES, J. D., 1959, *Disc. Faraday Soc.,* **27,** 149.

MYERS, J., 1963, *Nat. Acad. Sc.-Nat. Research Council Publ.* No. 1145, 301.

MYERS, J., and GRAHAM, J. R., 1963, *Plant Physiol.,* **38,** 105.

PARK, R. B., and BIGGINS, J., 1964, *Science,* **144,** 1009.

PEARLSTEIN, R. M., 1964, *Proc. Nat. Acad. Sc.,* **52,** 824.

ROBINSON, G. W., 1964, *Ann. Rev. Phys. Chem.,* **15,** 311.

WITT, H. T., MÜLLER, A., and RUMBERG, B., 1963, *Nature,* **197,** 987.