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(Incorporating discussions with Kenneth Sauer, I.D. Kuntz, Jr. and P. A. Loach)

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ABSTRACT

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Further studies on the photoinduced electron paramagnetic resonance signals found in photosynthetic tissue as a function of wavelength, as well as temperature, have made possible a more precise definition of the nature of the primary quantum conversion act. These observations, taken together with new as well as older observations on the light-induced spectral changes in both bacterial chromatophores and green plant quantasomes, have allowed us to specify the place at which two distinct and separate quantum conversion electron transfer reactions occur in green plants.

The transfer from a chlorophyll aggregate to an acceptor substance occurs similarly in the green plants as well as the bacterial systems. The other act, the transfer of an electron from a donor system producing a highly oxidized hole to the chlorophyll aggregate, is limited to the green plant. This latter, highly oxidized material then collects its electrons ultimately from water/the production of oxygen. with

In the green plant, the spread in energy between the primary donor molecule in the second act and the primary acceptor molecule of the first act may be as much as 2 ev, providing for at least three, and possibly more, sites for the production of ATP and for the spontaneous passage of holes and of electrons from these primary donor and acceptor sites, respectively, to their ultimate sites in molecular oxygen, on the one hand, and reduced pyridine nucleotide on the other.

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INTRODUCTION

One of the outstanding and possibly unique features of the process of photosynthesis as it occurs in nature today is the ability of the organism, either green plant or bacterium, to utilize a quantum of energy of the order of 38,000 calories for green plants and 30,000 for the bacteria to accomplish an ordered chemical transformation at room temperature with a relatively high degree of efficiency. When we remember that the apparatus which accomplishes this is of labile organic construction and that the thermal reactions which can be performed by such a system rarely, if ever, involve energy changes higher than 10,000 or 15,000 calories, it is an impressive accomplishment indeed to be able to manipulate a package of energy two or three times that size without damage to the apparatus and in a highly directed and specific way.

The ultimate products of this energy transformation have long been known to us in the form primarily of carbohydrate and oxygen, but, of course, including all of the plant substances. In fact, it is currently possible to describe some more immediate products of this energy conversion process in terms of more transient specific energy-storing materials. To be particular, we have every reason to believe that two such energy-storing inter-

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mediates which can be used to produce the final, or more long term, storage materials are reduced pyridine nucleotide and adenosine triphosphate. It may turn out that other transient energy-bearing chemical intermediates might be still closer to the energy transformation step itself.

At this point it is perhaps worthwhile to define, as nearly as we can, the properties of the energy-bearing intermediate(s) which we will consider as the earliest form of chemical energy into which the electromagnetic quantum may be converted. Such a material would be the first chemically definable compound in thermal equilibrium with its environment, but, quite clearly, not in chemical equilibrium with it, since under such a definition, oxygen itself could not be evolved.

We will consider the primary quantum conversion act, then, as that act, or sequence of events, following the absorption of the electromagnetic quantum and terminating with the appearance of a thermally relaxed chemically defined individual which may then proceed by direct thermal work-performing reactions to produce the next transient and, finally, the ultimate products of photosynthesis.

Under such a definition, an electronically excited state of a molecule, or array of molecules, such as might result from the primary absorption of a quantum of light, would not be considered as a chemical entity distinct from the parent material before light absorption. Only after the energy stored in this electronically excited state is transformed into new chemical species, which can then proceed to react, or interact, with its environment along thermodynamic principles would we consider the quantum conversion process accomplished. All succeeding reactions from these initial chemical species would, of course, be dark reactions.

Very early in the considerations of theories of photosynthesis it was recognized from the nature of the ultimate reaction that an oxidation and a reduction must be involved. For some time, the earlier proposals involved a direct transformation of the electronic excitation into the energy of atomic rearrangement, resulting in the transfer of hydrogen from water to carbon dioxide. There have been many varieties of this proposal. However, it remained for the brilliant analysis of van Niel on the comparative biochemistry of the photosynthetic process throughout the scale of living organisms to simplify the primary quantum conversion act into the production of a primary transient oxidant and a primary transient reductant.[1] These could then go about their separate ways, the reductant ultimately converting the carbon dioxide to the level of carbohydrate and the oxidant converting some suitable substrate, in the case of the bacteria, to an oxidized form, or ultimately being eliminated as molecular oxygen in the higher green plants.

This separation of oxidant and reductant was formulated by van Niel in terms of [OH] and [H] as representative symbols of the oxidant and reductant, respectively. In green plant photosynthesis, these two fragments would ultimately be derived from water. However, the essential feature is the primary production of oxidant and reductant, and in physical terms this means the production of a molecule, or species, avid for electrons, frequently represented by $\oplus$ or "hole", and a species generous with its electrons, i.e., with a relatively high electron pressure, most readily represented by $\ominus$ or simply $\ominus$.

How these two particles, or species, which would be produced as a result of the conversion of 30 to 40 kcal of energy might be separated

from each other so as not to back react represents one of the problems. Any mode of reaction, such as molecular rearrangement or dissociation, which might be used to store the 30 or 40 kcal must, of necessity, be so arranged that the product (or products) does not immediately revert to its initial state with the evolution of the stored energy either in the form of electromagnetic radiation or as heat. This requires that either a suitable energy barrier be interposed between the primary products and the initial state, or that the primary products are effectively separated from each other physically so that the recombination is statistically improbable.

The interposition of a barrier of any appreciable size would require the use of such a large fraction of the initially absorbed energy quantum to overcome it that the total energy stored in the process must, therefore, be a relatively small fraction of the quantum absorbed. Here the relatively high efficiency of the overall process limits us, and so we turn to the other alternative, namely, effective separation of the reaction products. This can be most easily accomplished if the reaction products are not massive atoms, but only electrons. We are thus led to the obvious suggestion that the primary quantum conversion act involves a separation of electrons from the "holes", or positive charges, which they leave behind in the molecules from which they come, a theoretical suggestion made very early by Katz.[2] It has been elaborated independently in our laboratory for similar theoretical reasons,[3-5] and based upon model experiments[6-8] and direct biological observation in recent years. A good deal of evidence has been accumulating in the last half dozen years that this is indeed the case.[9-12]

With the discovery of cytochrome f in the green tissues of plants by Davenport and Hill[13], Hill was even able to suggest that the separation took place in two distinct quantum steps.[14,15] The first one led to the reduction of the cytochrome associated with the production of a high level oxidant and the second ultimately to the oxidation of cytochrome with the concomitant production of a strong reducing agent.

Experimental evidence for such a process has since been accumulating. That the illumination of the photosynthetic apparatus of either green plant or bacterium would result ultimately in an electron transfer reaction was first seen in the results of Lundegardh[16] and Duysens.[17,18] They demonstrated by differential spectrophotometry that the illuminated plant, or particle, carried more oxidized cytochrome than did the corresponding plant or particle kept in the dark. Since then, this type of experiment has been broadly expanded in many laboratories.

However, it remained for another type of observation to show unequivocally that the absorption of light by the apparatus of any photosynthetic organism resulted in the transport of an electron from a paired condition at one site to an unpaired condition at another. Such an observation would distinguish between the transport of one electron from the transport of a pair. The unpaired electron should make itself apparent by virtue of its paramagnetism, and with the appearance of microwave techniques for the observation of electron paramagnetic resonance and with the high sensitivity it provided, it was possible to demonstrate just such a process.[19,20]

We will be concerned with the information that can be obtained by such measurements in conjunction with other physical and chemical parameters that can be varied, as well as the relationship of these magnetic changes to the optical changes upon illumination, which are many and varied.

EXPERIMENTAL RESULTS

Electron Spin Resonance Experiments[21]

When photosynthetic tissue, suitably prepared, is illuminated in a cavity of an electron paramagnetic resonance spectrometer, it is possible to see the electron paramagnetic resonance of the unpaired electrons that are produced. Such signals are produced in whole spinach chloroplasts, both at 25°C and at -150°C at a rapid rate. The rise time is faster than the response time of the instrument in both cases. The signals so produced are shown in Figure 1 for whole spinach chloroplasts.[20] Signals produced in the whole organism of Rhodospirillum rubrum maintained at various temperatures and illuminated with white light are shown in Figure 2. The signals produced in the isolated chromatophores from these organisms are identical in shape and form and other physical properties, insofar as we have been able to determine.

That these unpaired spins are produced by light absorbed by the corresponding chlorophylls is shown in the action spectra for green plant quantasomes reproduced in Figure 3[22] and in Rhodospirillum rubrum chromatophores shown in Figure 4.[22] It is interesting to note the possibility of the existence of an inflection point on the long wave side of the absorption of the quantasomes corresponding to what might possibly be a difference in the action of light at wavelengths somewhat longer than 700 mu.

It has been possible to separate the green particle EPR signal into two components, as shown in Figure 5a. There can be seen in the whole chloroplasts two distinct signals. One of them is a sharp signal with a very rapid growth and decay time at room temperature, and the other is a much broader one with a slow growth and decay time at room temperature. It has been possible, by suitably fracturing the chloroplasts, not only to separ-

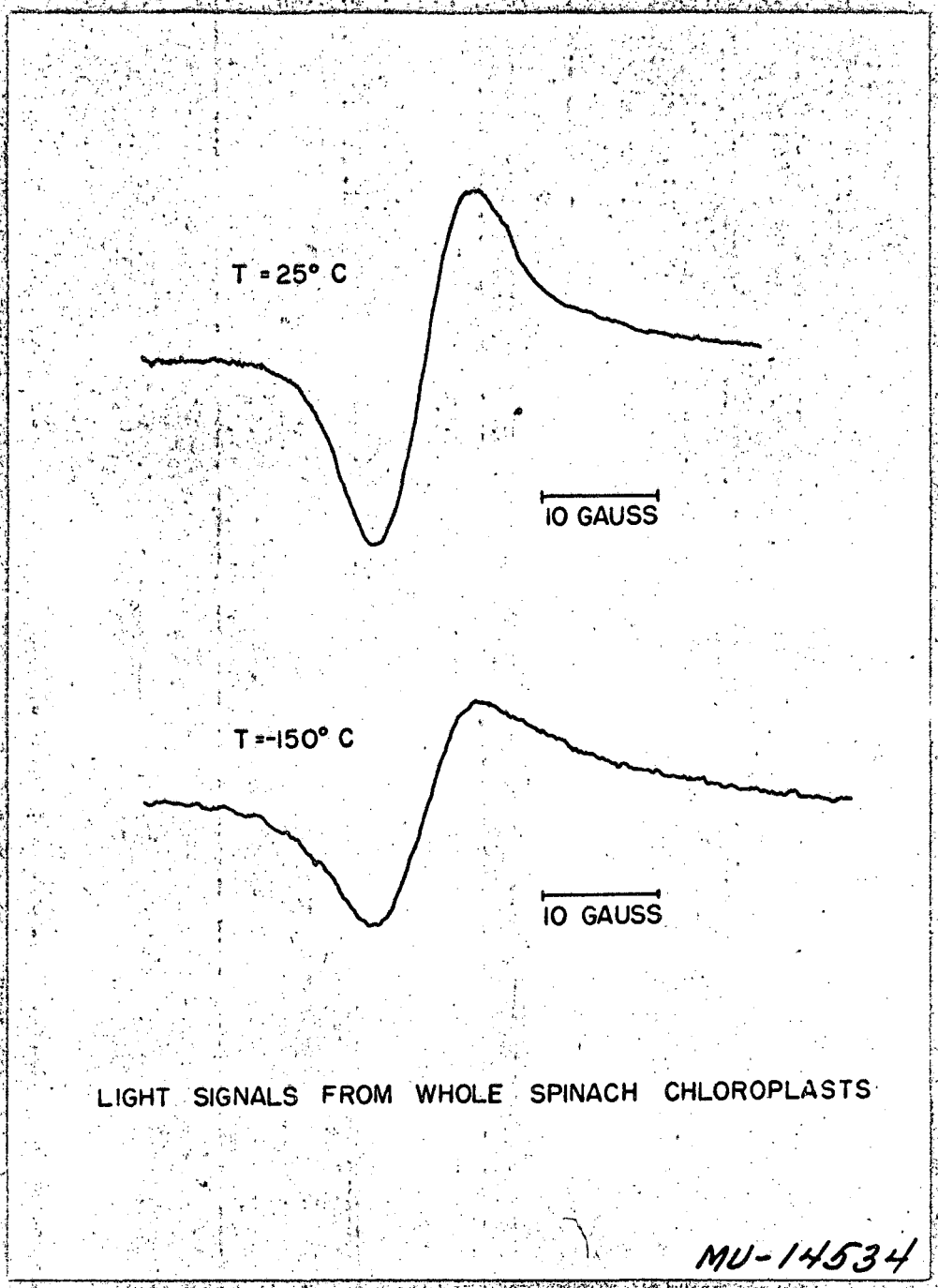

Figure 1. Light signals from whole spinach chloroplasts.

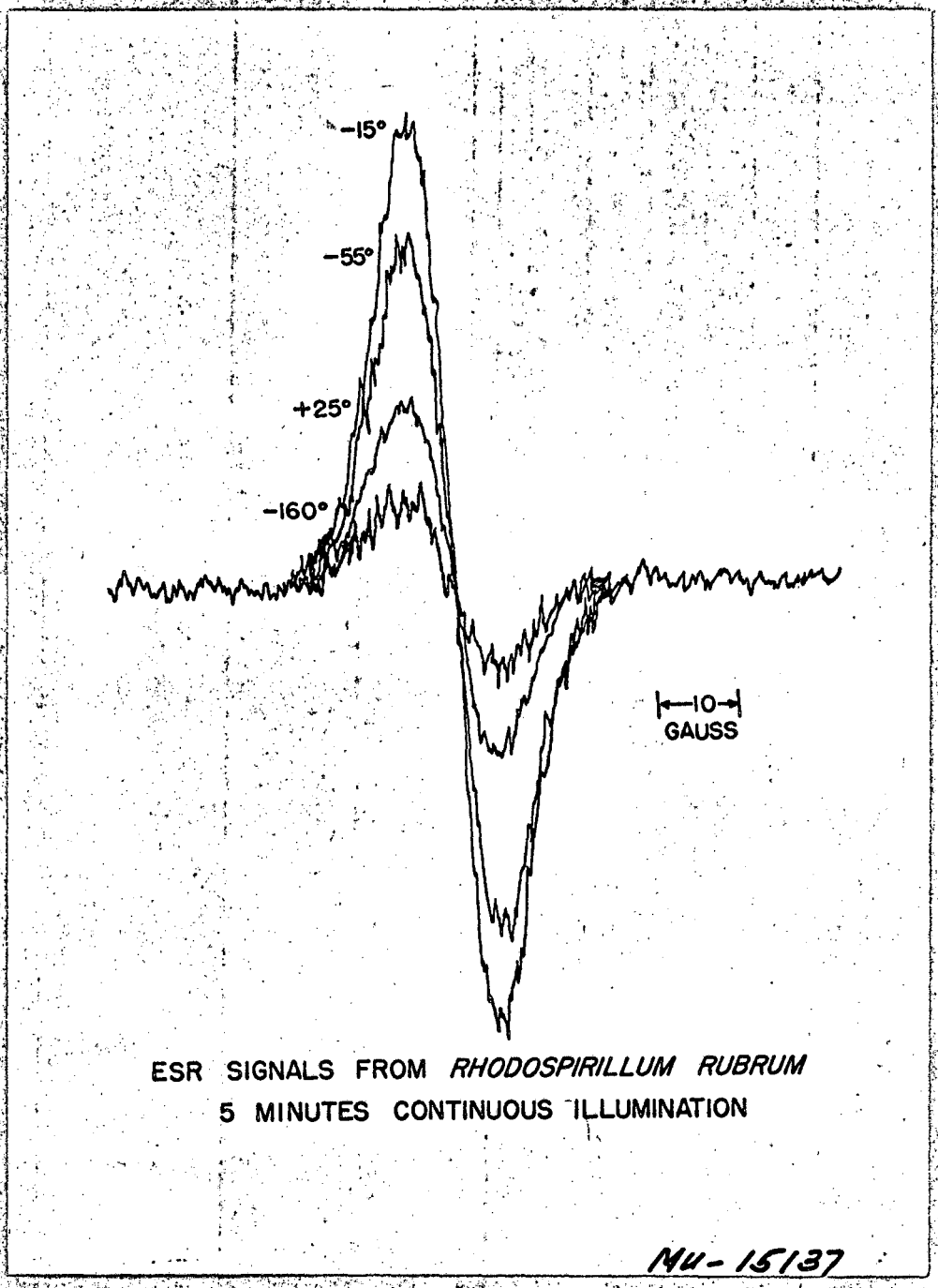

Figure 2. EPR signals from Rhodospirillum rubrum; 5 minutes continuous illumination

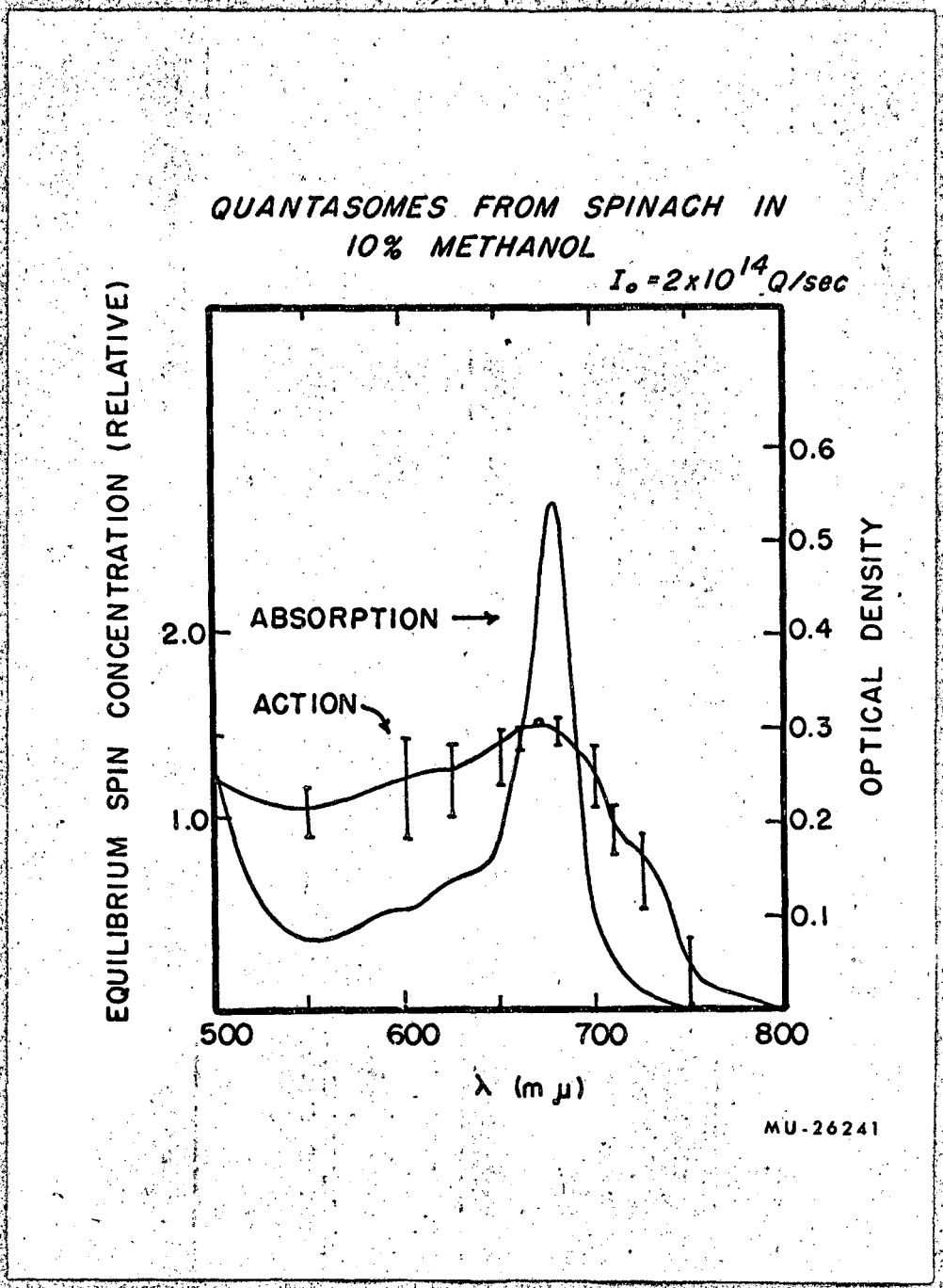

Figure 3. Absorption and action spectra of quantasomes from spinach chloroplasts.

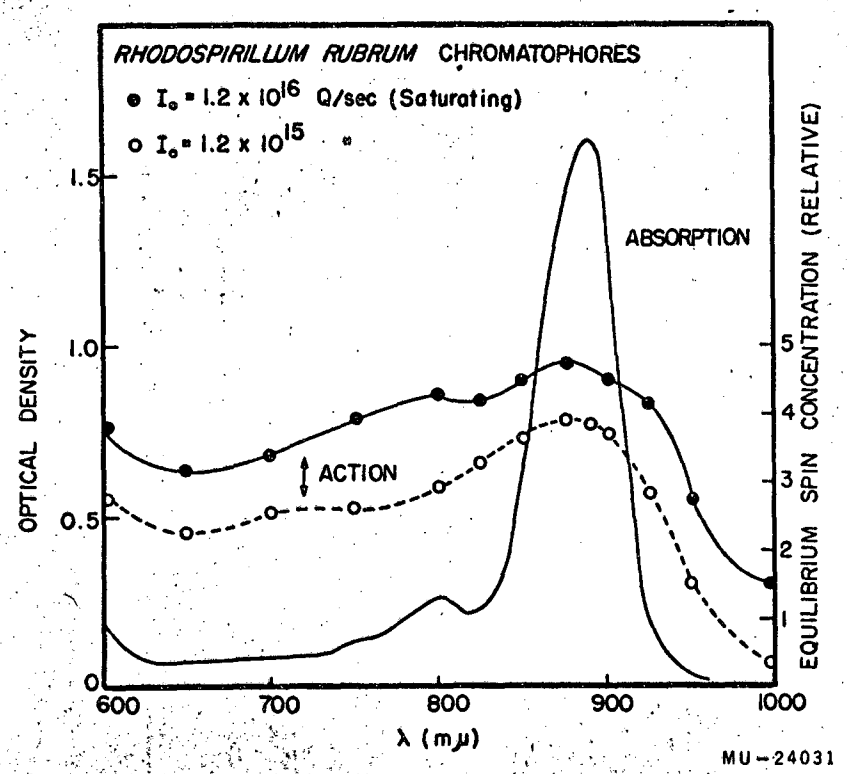

Figure 4. Absorption and action spectra of chromatophores from Rhodospirillum rubrum.

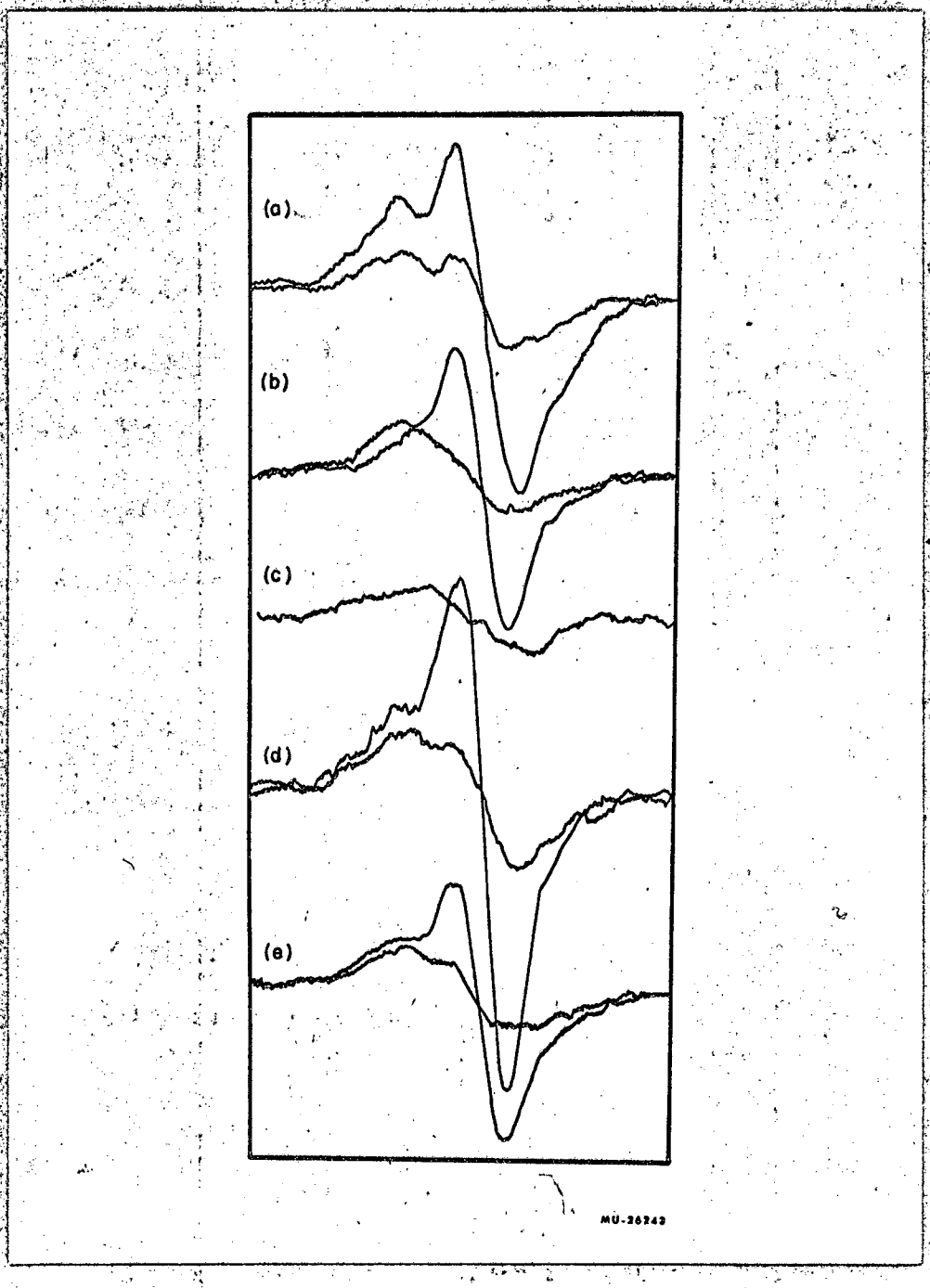

Figure 5. EPR (dark signal and light signal, if any) in several green particle fractions.
(a) Whole chloroplasts; (b) quantasomes plus soluble protein; (c) colorless soluble protein bleached from whole chloroplasts; (d) washed quantasomes; (e) quantasomes plus soluble protein.

In each case, the trace containing the larger signal is the one produced in the light. The magnetic field increases to the right. Defining a basic chlorophyll concentration of C_o as 15 mg of chlorophyll/ml of sample, the chlorophyll concentration in the samples containing pigmented particles is: (a) $\sim$ 3 C_o; (b) $\sim C_o$; (d) $\sim$2 C_o; (e) $\sim C_o$

ate them into a green particle containing all, or almost all, of the chlorophyll (the quantasome),[23] and a soluble component, but also to show that the sharp signal remains associated with the quantasome particle while the broad one is washed out with the soluble component and can be observed separately, as shown in Figure 5c.

Temperature Effects

Very early in the work on the observation of the production of unpaired spins in photosynthetic tissue it was recognized that one physical variable which would help to distinguish between the production of ordinary chemical free radicals involving either the separation of atoms or at least the diffusion of molecular particles, was the temperature. Quite clearly the ability of such signals to appear at very low temperatures, at least as low as liquid nitrogen temperature and perhaps lower, would imply the physical nature of the mechanism for forming them.

Therefore, the appearance of these signals was examined as a function of temperature, almost down to liquid nitrogen temperatures. Thus in Figure 6 we see that the rise time of the spin produced in whole spinach chloroplasts is still faster than the instrument response time, even at the low temperatures. It is important to note, however, that in this material the signal once produced at low temperatures does not decay until the material is warmed.

When the temperature is lowered on the chromatophores from R. rubrum the rise time is again unchanged within the limitations of the instrument (Figure 7). However, there is an important difference in this organism from the green plant material, namely, that while the decay of the signal is complex at room temperatures, that is, showing a number of different decay constants, by the time it reaches -112°C and down to -150°C, all of the slow decays have been frozen out; all that remains is a decay time more rapid than the instrument can follow. In other words, there exists in the chromatophores

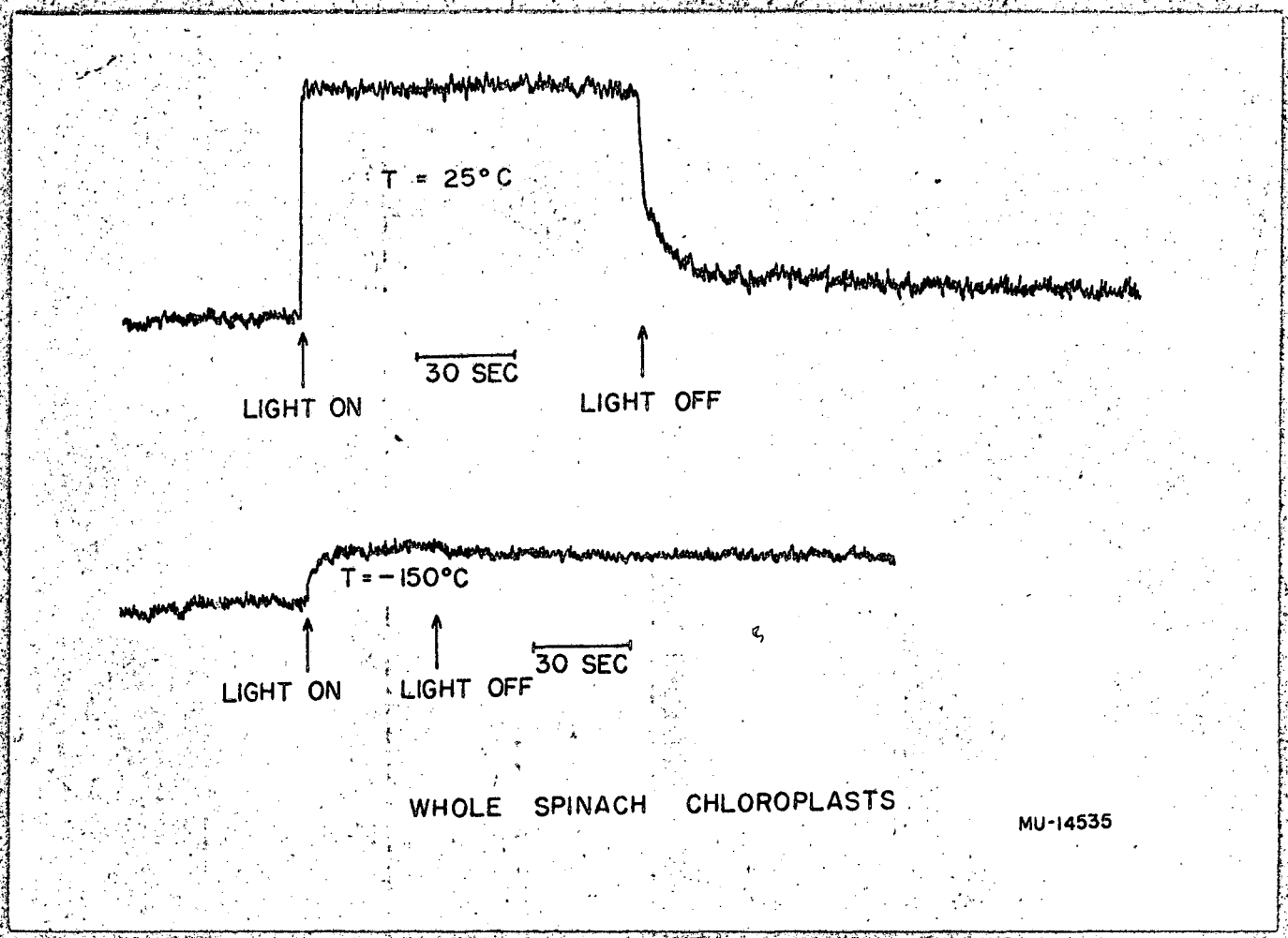

Figure 6. Growth and decay curves from whole spinach chloroplasts.

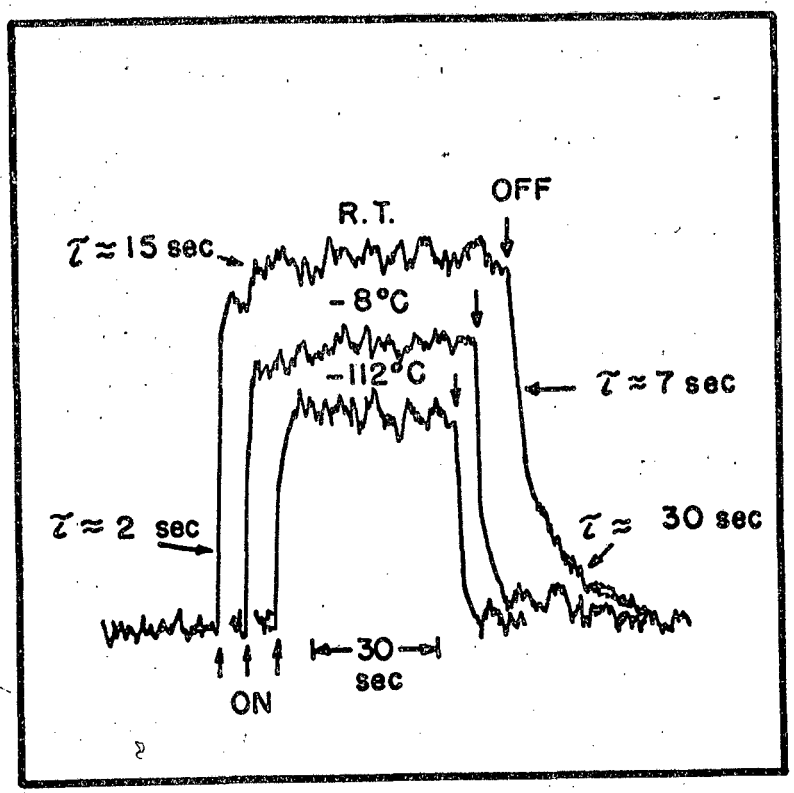

Figure 7. Rise and decay of the electron paramagnetic resonance in the chromatophores of Rhodospirillum rubrum

a system for the production of unpaired spins at low temperature which appears to be kinetically temperature independent, both for its formation and its decay.[22]

Optical Density Changes

An examination of the kinetics of the color changes in both of these materials (chromatophores and quantasomes) has been underway in several laboratories, particularly those of Duysens, of Witt, of Chance, and, more recently, of Kok. It was observed by Chance and Nishimura that the color changes in the region 550, 523 and 430 mu induced by illumination could be achieved at liquid nitrogen temperature quite as rapidly as they could at room temperature.[24] However, they did not decay at liquid nitrogen temperture. A similar change at around 550, 430 and 405 mu induced by illumination of chloroplast material has also been induced at liquid nitrogen temperature but they do not recover, i.e., the optical density changes are "frozen in."[25] These changes have been called cytochrome oxidations in both cases. It is therefore clear that at least in the case of the purple bacteria (Chromatium, Rhodospirillum rubrum, Rhodopseudomonas spheroides)[26] the unpaired spin signal which is reversible at low temperature does not reside in the cytochrome.[26]

Some color change, however, can be induced by illumination in purple bacteria which is reversible even down to 1°K. Arnold and Clayton observed an optical density increase at approximately 420 mu in chromatophores from Rhodopseudomonas spheroides which was reversible down to 1°K.[12] Further studies by Clayton on purple bacteria have demonstrated that reversible changes at around 430 mu can be observed without concomitant cytochrome changes.[27] It therefore appears certain that at least some of the optical density change observed in the 420 mu region is not due to cytochrome but to some other change resembling a simple physical electron transfer reaction.

While the electron spin resonance experiments have not yet been carried to this lower temperature, the fact that no change at all in either the signal or its kinetics has been observed on passing from -112°C to -150°C suggests that the situation will remain unchanged at lower temperatures. We are therefore prone to associate the unpaired spin which we have observed with the light induced reversible optical density change at 420 mu seen by Arnold and Clayton.

Redox Reactions

In an attempt to place the redox level of some of the constituents in the electron transport chain which seem to be here involved, the assumption has been made that an external redox couple could control the oxidation level of a component in the electron transport chain at the corresponding redox level. A variety of such couples has been used, ranging in potential from those having a high electron pressure, approaching that of pyridine nucleotide at -0.3 volt, to those having a high electron affinity such as ferricyanide with a potential of about +0.45 volt.

When bacterial chromatophores were treated with a variety of such redox systems, it was found that ferricyanide would induce optical changes in the chromatophores which resemble very closely those produced by illumination. A comparison of these optical density changes induced in the chromatophores of a carotenoid-less mutant of Rhodopseudomonas spheroides is shown in Figure 8, taken from the work of Clayton.[28] It seems quite clear that the major optical density decreases at 870-890 mu are indeed associated with the oxidation of chlorophyll.

A similar relationship between the light-induced optical changes and those induced by ferricyanide on the green particles (chloroplasts or quantasomes) has been observed by Kok and Hoch[29] and also by Witt.[25]

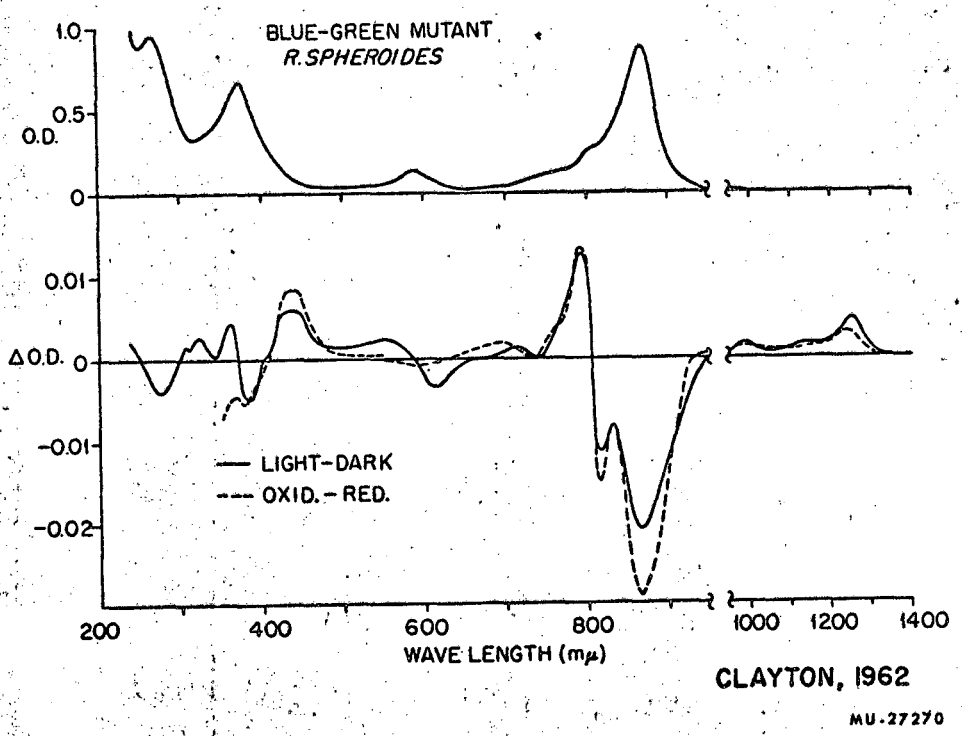

Figure 8. Optical density changes induced by ferricyanide in chromatophores of carotenoid-less mutant of R. spheroides (Ref. 28)

Here the change is a decrease in optical density at 705 mu as well as a decrease at 430 mu. The fact that the light-induced optical density changes are reversible at low temperatures in the chromatophores and not reversible at low temperatures in the quantasomes, thus corresponding to behavior of the unpaired spins in both cases, is added evidence that they are indeed due to the same, or closely related, species in each case, namely, the chlorophyll.

Finally, it has been found that the electron spin signal can also be induced in these two particles by oxidation with ferricyanide. This is probably the same process as that reported for particles from a red alga by Kok.[30] Since the oxidation of the chlorophyll could produce a Chl^+ radical or "hole" in an ordered array, it would appear that the optical signal and the spin signal might, to a first approximation, be due to the formation of Chl^+. Further evidence can be found in the fact that when the Chl^+ is produced chemically by ferricyanide, as evidenced either by the optical density change or by the electron spin resonance signal in the dark, the magnitude of the light-induced optical changes and the light-induced EPR signals is diminished.

In fact, when a quantitative estimate is made of the amount of oxidation-produced EPR signal as a function of the ferro-ferricyanide ratio (and thus the electrochemical potential) in the medium and compared with the amount of additional unpaired spin that can be induced by the light on the same system, a complementarity between the two is exhibited, as shown in Figure 9.* The point for the production of the dark signal up

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* We are grateful to Dr. P. A. Loach for collaborating in the establishment and measurement of the potentials in these experiments.

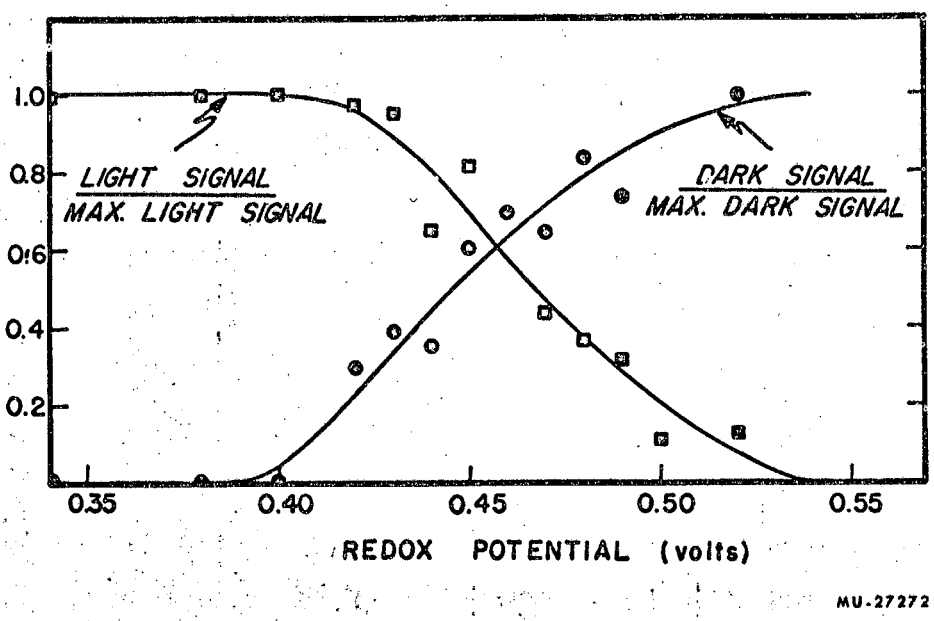

Figure 9. Redox titration of the chemically-induced and photo-induced EPR in quantasomes from spinach chloroplasts

to half its maximum value corresponds approximately to the point for the reduction of the light-induced signal to half of its maximum value, both of them lying at an apparent oxidation-reduction potential of about +0.46 volt. A similar value was obtained in particles from red algae by Beinert, Kok and Hoch.[30]

A corresponding complementarity would be expected to exist in the production of the spectral changes induced by oxidation with the same change introduced by illumination. Experimentally the magnitude of the change in optical density at 700 mu and 420 mu produced by illumination of the quantasomes decreases with increasing degree of oxidation determined by the ferro-ferricyanide ratio in the medium.*

Complementarity in electron spin signal has also been observed in chromatophores, the data for which are shown in Figure 10. A complementarity in the light-induced optical density changes also exists here.*

An additional feature appears in the chromatophores under reducing conditions. Under these conditions the light-induced spin signal is suppressed (Figure 10). Similarly, the light-induced optical density increase of the chromatophores at 430 mu is also suppressed by this reducing medium.* A quantitative correlation between the two has not yet been made.

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* I. D. Kuntz, Jr. and P. A. Loach, unpublished observations in this laboratory.

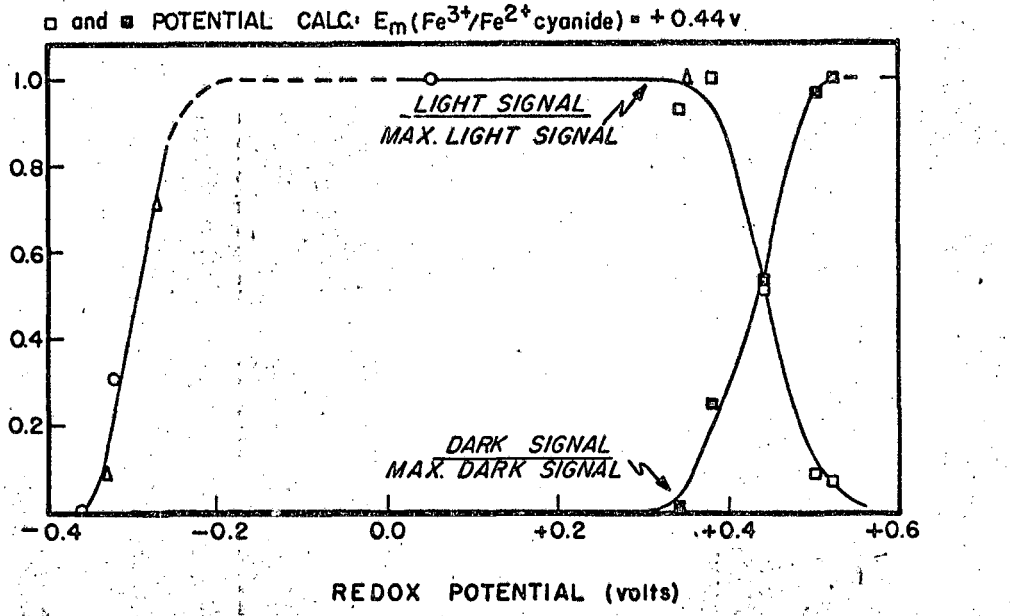

Figure 10. Redox titration of the chemically-induced and photo-induced EPR in chromatophores from R. rubrum

For the moment, then, we will presume that the oxidation-induced EPR signal and optical density changes are due to the removal of an electron from chlorophyll, or bacteriochlorophyll as the case may be, leaving behind a Chl^+ radical ion situated among neutral chlorophyll molecules. It may thus be called a positive "hole." Since the light is not sharply monochromatic and since the two presumed absorption wavelengths in green material are not so widely separated, it is possible that at least part of the light-induced EPR signals here might be due to a second primary species, e.g. Chl^-, not to speak of the secondary possibilities. The EPR signal would be expected to be very similar to that of $BChl^+$.[31]

DISCUSSION

The fact that the light-induced spin signal, as well as the light-induced optical density changes in the chromatophores seems to be reversible down to the very lowest temperatures (optical density change down to 1°K; electron spin signal down to 77°K) requires first that the electron transfer reactions which produce these species to be simple physical transfer reactions not involving the migration of molecular species, and, secondly, that the return to the original condition, both with respect to optical density and spin signal, go by a path corresponding to the reversal of its formation. Thus, we require the energy level for the electron acceptor in the case of the formation of the chlorophyll positive ion radical, or hole, as being separated from it (the hole) by very nearly the full value of the quantum of energy which is accomplishing the electron transfer. We are thus constrained to place the electron acceptor potential at a very negative value, perhaps even as low as -1 volt, or more (Figure 11). Direct evidence for a similar wide separation between donor and acceptor in a second quantum act, which would be involved in the neutralization of the hole, is not yet available.

While the action spectrum for spin production does show some inflections on the long wave side, the spin signal itself is not sufficiently variable with wavelength for us to be able to specify the existence of two different kinds of unpaired spins produced by two different colors of light. However, the accumulating literature seems to involve a second light act in the green material. It stems from the early suggestions of Hill[14,15] and the experimental observations of Emerson[32] and more recently

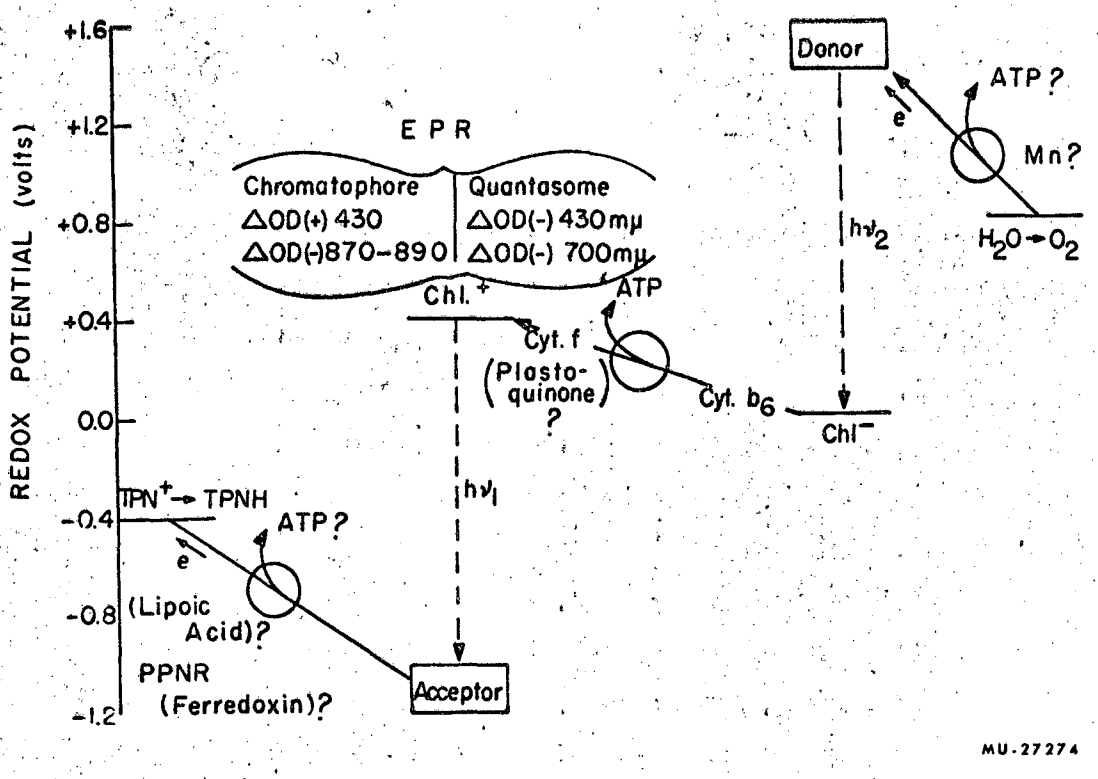

Figure 11. Schematic diagram showing the approximate redox relationships of some species proposed as involved in the primary quantum conversion act(s).

of Kok[30] and Witt[33] and Duysens.[34] The evidence prompts us to introduce another electron transfer act for which the product in this case is Chl^- radical ion, also imbedded in a matrix of neutral chlorophyll molecules, thus corresponding to a conduction electron. Here efficiency arguments to allow for a quantum requirement of less than 8 would seem to require the donor molecule for this electron transfer act to have a potential in the vicinity of +1.5 volts, thus making more efficient use of the quantum by providing an additional site for ATP production.

We thus arrive at a modification of the two-quantum proposal of Hill[14,15], and of Witt[33], Kok[30], and of Duysens[34], in which the primary donors and primary acceptors at each end of the scale are further apart than has heretofore been supposed, and thus provide two additional possible sites for ATP production than does Hill's scheme. The first of these sites would be at energy available in the passage of the electron from the primary acceptor, at -1 volt, down to the ultimate reducing agent, such as TPN, at about -0.3 volt, perhaps passing ghrough either such cofactors as lipoic acid, PPNR[35] (ferredoxin), both, or several others on its way.[36,37] The second site would be the one proposed by Hill and would lie along the passage of the electron from the first acceptor, at $\sim$ 0.0 volt (Cyt b_6, plastoquinone), to the Cyt *f* at $\sim$ 0.4 volt, when it would enter the second pigment system. It is interesting to note in this connection the recently reported probable value for the number of ATP molecules produced by electron transfer in bacterial chromatophores as being 2.[38] The third site for ATP production would be at the other end of the scale, during which the electron passes from

water to the primary donor, through as yet unknown cofactors, and among which we may expect to find a manganese function.[39] The ultimate result of such a scheme would be the separation of the oxidant and reductant to the levels of oxygen and pyridine nucleotide and the production of three ATP molecules through the action of two successive quanta, as shown in Figure 11.

If the quantum requirement for overall photosynthesis can indeed be made less than 8, then some of the excess ATP molecules could be used to promote the reductant-oxidant separation at some point in the potential scheme (Figure 11) and thus reduce the demand for quanta for this purpose.[40]

(Figure 12)

A physical depiction of the entire quantum conversion process can now be formulated in terms of the absorption of light by the pigment, followed by exciton migration to the site of electron transfer.[28,41,42] In the case of the bacteria, this electron transfer would involve the production of a $BChl^+$ radical ion and a reduced acceptor at high reduction potential. The $BChl^+$ radical ion could migrate by hole migration to a site where it may recover its electron from such a donor as Cyt c_2, which is common in the bacteria.[43] In the green plant, a second chlorophyll system is provided which undergoes similar excitation and exciton migration to a site of electron transfer. But, in this case, the electron transfer is from the donor at some potential higher than that of molecular oxygen -- that is, equal to or greater than one volt -- and the electronic conduction process carries the resulting electron in the chlorophyll system to the site of its deposition at the connecting link between the two chlorophyll systems.

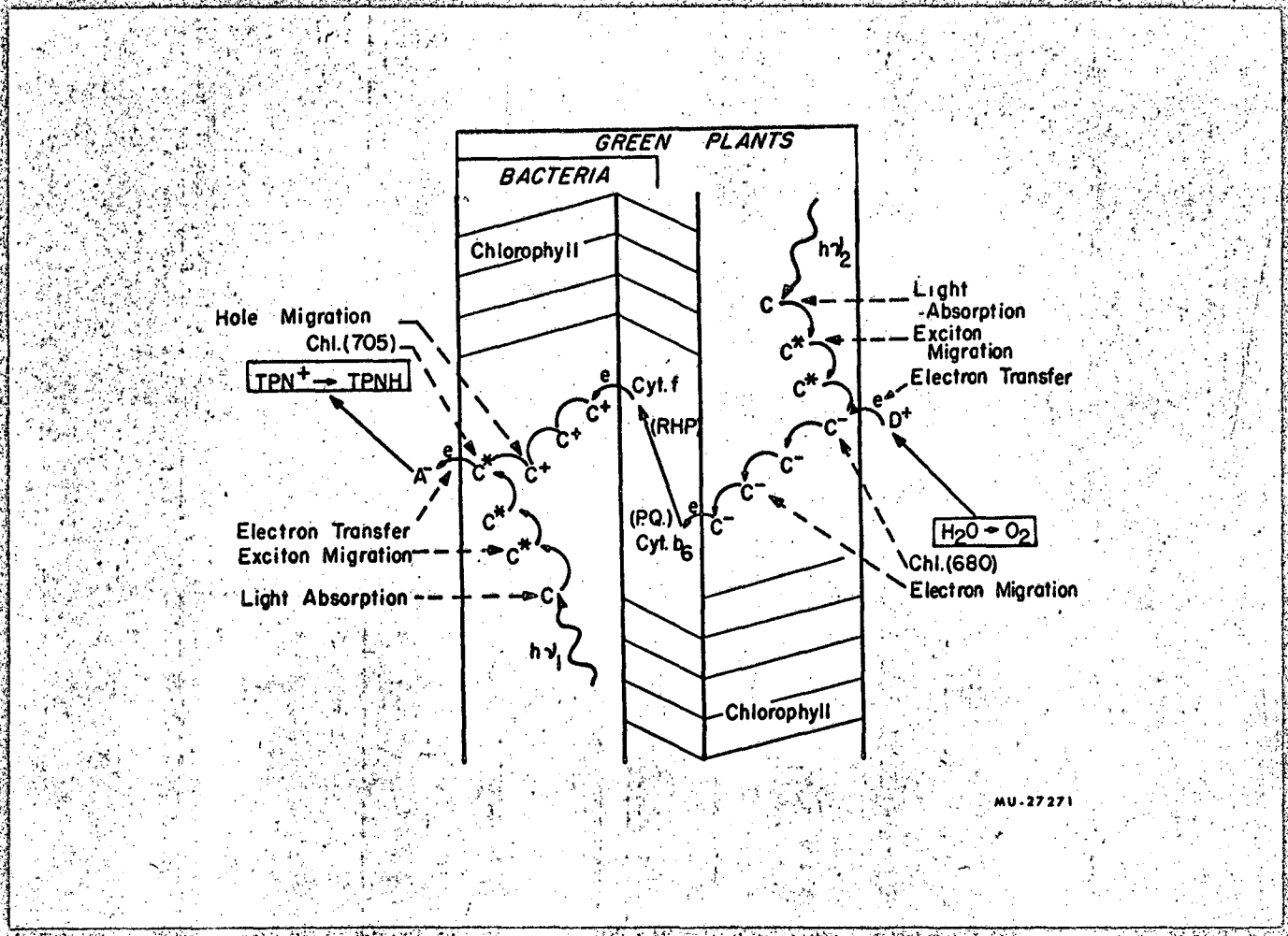

Figure 12. A proposal for the primary quantum conversion act(s)

We have thus expanded a system originally proposed some years ago, at which time we could not adequately distinguish between electron migration or hole migration in the chlorophyll array.[11] In this present proposal it now appears as though in the green material both systems are possible transport systems. The primary quantum conversion and the separation of oxidant and reductant would thus depend in both pigment arrays on semiconduction mechanisms -- hole migration on one side and electron migration on the other. While the low temperature reversibility of spin signal and optical density changes is strong evidence for the hole migration system, corresponding evidence is still lacking for the electron migration system.

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