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COMMENTS ON FRANCK'S THEORY OF THE PRIMARY QUANTUM
CONVERSION PROCESS IN PHOTOSYNTHESIS

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Berkeley, California

COMMENTS ON FRANCK'S THEORY OF THE PRIMARY QUANTUM CONVERSION
PROCESS IN PHOTOSYNTHESIS*

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Recently, Professor Franck has proposed a theory which purports to explain the function of chlorophyll in the primary quantum conversion process in photosynthesis.¹ The theory involves the formation of a chlorophyll in an excited singlet state by the absorption of a quantum of light, the formation of triplet-state chlorophyll by a highly probable intersystem crossing, and the conversion of the triplet-state chlorophyll into a "doubly-excited" triplet state by a resonance transfer process involving another excited singlet-state chlorophyll molecule. This "doubly-excited" molecule is then directly involved in the chemical transformations by virtue of its having become associated, prior to its formation, with the enzyme and the acceptor molecule. The photosensitized

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chemical reaction then involves the transfer of an H atom and an hydroxyl group and the formation of a double bond in the chlorophyll molecule.

While Professor Franck's theory possesses a number of theoretical advantages from the point of view of photosynthesis, there are, in the light of present knowledge, at least two difficulties which the present author feels should be pointed out. First, the most recent data^{2,3} indicate that the lifetime of the first excited singlet state of chlorophyll is of the order of $1 - 2 \times 10^{-9}$ seconds in vivo and that the quantum yield of fluorescence is only 2 - 3% in vivo. Thus, if conversion to the triplet state is going to account for such a low fluorescence yield, the time constant for this conversion process must be of the order of 10^{-11} seconds. In other words, the lifetime of the state which is funneled into the photochemical pathway has this magnitude. According to some calculations by Rabinowitch,³ resonance transfer over only from 1 - 100 chlorophyll molecules could occur in this time. Therefore, Franck's theory would require that a photochemical act could be carried out only if two excitations occurred within a volume occupied by approximately 100 chlorophyll molecules⁴ during the lifetime of the first excited triplet state of chlorophyll.⁵ This would necessitate a minimum light intensity of the order of 10 einsteins/mole chlorophyll/minute⁶ to achieve an efficient yield of photosynthesis. It is known that photosynthesis will proceed efficiently in light intensities of at least three orders of magnitude less than this.⁷

The second difficulty involves the lifetime of the "doubly-excited" state. Inasmuch as the separation between first excited singlet state and second excited singlet state in chlorophyll a is approximately 8000 cm^{-1} , it can easily be seen that the "doubly-excited" state must correspond to a

relatively highly excited triplet state if resonance transfer is to occur. At high energy levels, quantum theory predicts that the states will be correspondingly closer in energy than at lower levels of excitation.⁸ Thus, internal conversion between triplet states should be very rapid, probably occurring with a lifetime of the order of 10^{-13} seconds or less (about the period of a molecular vibration), if one extrapolates from the rates of internal conversion between the two lowest excited singlet states in organic molecules⁹ (which have much larger energy separations than the triplet states considered here). It is very unlikely that an enzymatic reaction involving group migration and double bond formation could take place in times of this order of magnitude. Furthermore, even if one concedes that the enzyme and the chlorophyll triplet are bound together strongly enough so that energy absorbed in the latter is available almost immediately to the former, one loses the favorable energy level juxtaposition that is necessary for an efficient energy transfer from the chlorophyll singlet to the chlorophyll triplet.¹⁰

A theory of the primary quantum conversion process which provides for a "storage" of the electromagnetic energy contained in more than one light quantum is to be found in the papers of Katz,¹¹ of Bradley and Calvin,¹² and of Tollin, Sogo and Calvin.¹³ This scheme retains the advantages possessed by a "doubly-excited" state without involving the difficulties mentioned above.

LIST OF REFERENCES

1. J. Franck, *Daedalus*, 86, 17 (1955); also in "Research in Photosynthesis," Proceedings of the Second Gatlinburg Conference on Photosynthesis of the National Research Council, October 25-29, 1955, edited by H. Gaffron et. al., pp. 19-30, 142-146, Interscience Publishers, Inc., New York (1957).
2. S. S. Brody and E. I. Rabinowitch, *Science*, 125, 555 (1957).
3. E. I. Rabinowitch, *J. Phys. Chem.*, 61, 870 (1957).
4. This figure represents only an approximate upper limit to the chlorophyll unit within which two excitations must occur. A more accurately ascertained figure would undoubtedly be lower due to the random nature of resonance transfer processes.
5. This lifetime is of the order of 10^{-4} seconds in solution (R. Livingston, G. Porter, and M. Windsor, *Nature*, 173, 485 (1954)). The corresponding value for in vivo chlorophyll is unknown. However, flashing light studies (R. Emerson and W. Arnold, *J. Gen. Physiol.*, 16, 191 (1932)) indicate that, if the triplet state is involved in photosynthesis, its lifetime cannot be longer than approximately 0.1 second. Therefore, we have used this value for the triplet-state lifetime in the calculation below.
6. $(2 \text{ quanta}) (10^{-2} \text{ molecules}^{-1}) (6 \times 10^{23} \text{ molecules/mole}) (10 \text{ seconds}^{-1}) (60 \text{ seconds/minute}) = 7.2 \times 10^{24} \text{ quanta/mole/minute} \approx 10 \text{ einsteins/mole/minute.}$
7. E. I. Rabinowitch, "Photosynthesis," vol. II, part 1, p. 1135, Interscience Publishers, Inc., New York (1951).
8. This is readily seen in chlorophyll a which has a ground state to first excited singlet state separation of $14,700 \text{ cm}^{-1}$ and a first excited singlet to second excited singlet separation of only 8000 cm^{-1} .

9. M. Kasha, Discussions Faraday Soc., 9, 16 (1950).
10. The overlapping of the energy levels of the singlet and triplet of chlorophyll is none too favorable even for the isolated molecules in that the far red band of the triplet, if it exists at all, is very much weaker than the red band of ground state chlorophyll (R. Livingston in "Research in Photosynthesis," Proceedings of the Second Gatlinburg Conference on Photosynthesis of the National Research Council, October 25-29, 1955, edited by H. Gaffron et. al., pp. 9, 11, Interscience Publishers, Inc., New York (1957)). Strong binding of the chlorophyll triplet would shift its absorption further into the red, thus decreasing the overlap between the energy levels of the singlet and the triplet.
11. E. Katz in "Photosynthesis in Plants," edited by W. E. Loomis and J. Franck, chap. XV, p. 291, Iowa State College Press, Ames, Iowa (1949).
12. D. F. Bradley and M. Calvin, Proc. Nat. Acad. Sci. U.S., 41, 563 (1955).
13. G. Tollin, P. B. Sogo and M. Calvin, New York Academy of Sciences Conference on Photoreception, Jan. 31 - Feb. 1, 1958, in press; for an earlier version see G. Tollin and M. Calvin, Proc. Nat. Acad. Sci. U.S., 43, 895 (1957).