REVIEWS OF MODERN PHYSICS VOLUME 16, NUMBERS 3 AND 4 JULY–OCTOBER, 1944

Spectra of Porphyrins and Chlorophyll*

E. Rabinowitch
Massachusetts Institute of Technology, Cambridge, Massachusetts

April 4, 1945

I

THE straight polyene chain and the closed porphin ring system are the two biologically most important chromophores in plant and animal world. The first one is encountered, e.g., in visual purple, and is thus of fundamental importance for the phenomenon of vision; it is also present in numerous pigments (carotenoids) which have an important function in photosynthesis, phototaxis, and other light induced biological processes. The importance of the porphin ring system is obvious from the fact that it is the basic structure of the animal blood pigments hemin and hemocyanin and of the plant pigments chlorophyll and bacteriochlorophyll, which are responsible for the synthesis of organic matter on earth.

The porphin system (Fig. 1) contains nine conjugated double bonds forming a closed 18-membered ring, somewhat similar to the 6-membered benzene ring. Two additional C—C bonds, whose positions differentiate the mesomeric or tautomeric structures 1A and 1B, are double bonds in porphin itself and in its mostly red or purple derivatives of the *porphyrin* class (to which hemin belongs); however, these double bonds are not parts of the all-round conjugated system, but are in a "unilateral" conjugation with this system. When one of these two "semi-isolated" double bonds is hydrogenated, the resulting compound (dihydroporphin) is green, and the same is true of most of its derivatives which are consequently called *chlorins*. The best known of these is chlorophyll. The hydrogenation of the second semi-isolated double bond leads to tetrahydroporphin and its derivatives, "bacteriochlorins" a representative of which is the bacteriochlorophyll; it, too, is green, but its spectrum is as characteristically different from that of chlorophyll, as the spectrum of chlorins is different from that of the porphyrins.

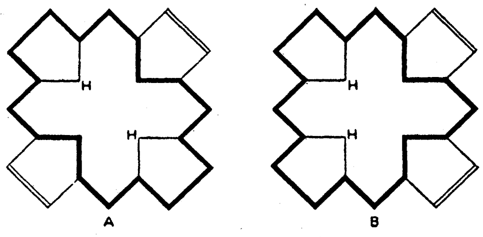

FIG. 1. The porphin system. A-diagonal form; B-lateral form. The heavy line represents an all-round conjugated system of nine single and nine double bonds. The four corner positions nearest to the center are occupied by nitrogen atoms; thus, the whole system can be derived from four pyrrol nuclei connected by four CH-bridges.

Figure 2 shows the structures of protochlorophyll *a* and chlorophyll *a*—two compounds which differ only by the presence in chlorophyll of two extra hydrogen atoms in nucleus IV; in other words, they represent a porphyrin and a chlorin with identical substituents. These substituents include, in addition to several alkyl groups, a magnesium atom in the center of the molecule, a vinyl group in nucleus I, a subsidiary 5-membered (cyclopentanone) ring V and two carboxyl groups esterified by two alcohols (methanol and phytol).

II

The absorption spectra of the porphyrins have a very typical pattern, illustrated by the

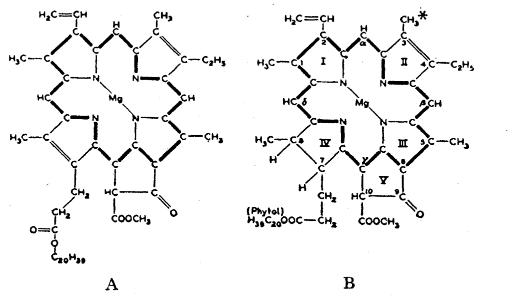

FIG. 2. Structural formulae of A-protochlorophyll *a* and B-chlorophyll *a* (after H. Fischer). Asterisk designates the CH_3-group which is replaced by CHO-group in chlorophyll *b*.

---

* Contribution No. 515 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, and Paper No. 14, Solar Energy Conversion Research Project.

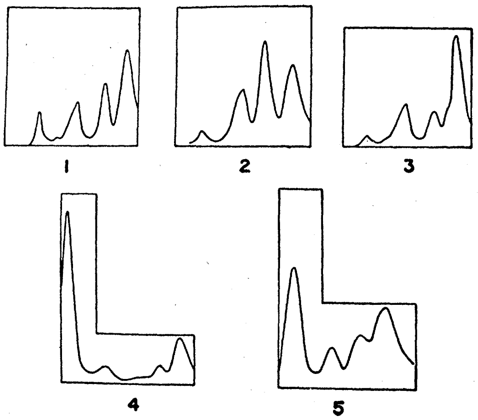

FIG. 3. Typical porphyrin and chlorin spectra (after Stern, reference 1). No. 1. *etio* type, No. 2 *rhodo* type, No. 3 *phyllo* type: porphyrin spectra. No. 4 *chlorin* type, No. 5 *rhodin* type: chlorin spectra.

schematic absorption curves No. 1, 2, and 3 in Fig. 3.[1] They all have four bands between 500 and 700 mμ, generally increasing in intensity from red to green, and a very strong band in the blue-violet region (not shown in Fig. 3; cf. for example, Figs. 8 and 13). The increase in intensity is particularly regular in the *etio* type; in the *rhodo* type the third band from the red is "too strong" (stronger than the fourth one); while in the *phyllo* type this band is "too weak" (weaker than the second one).

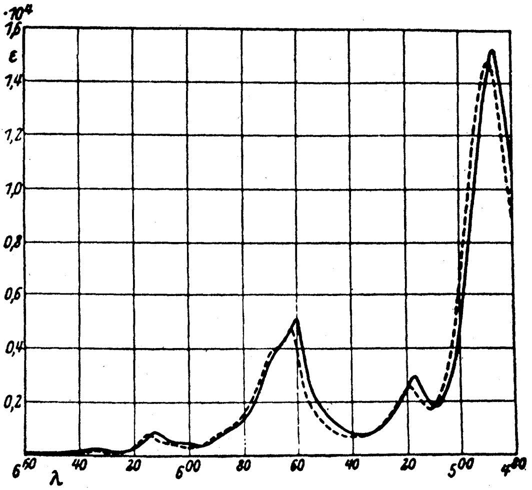

FIG. 4. Absorption spectrum of porphin (after Stern, Molvig and Wenderlein, reference 2); —— in dioxane and ------ in benzene.

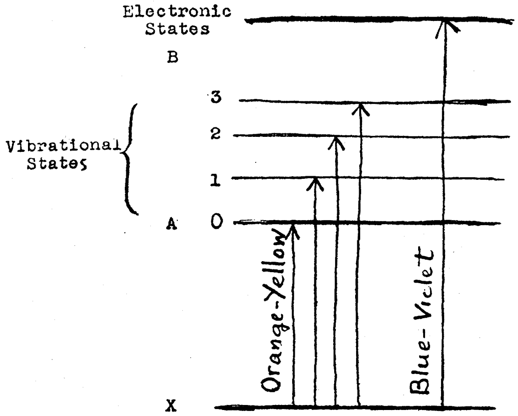

FIG. 5. The term system of porphin.

The parent substance of the whole class, porphin, has a spectrum of the *phyllo* type, shown in Fig. 4.[2] Table I gives the positions of the band maxima. The wave-number differences make it appear likely that the four bands in red, yellow, and green are vibrational bands corresponding to a common electronic transition; while the fifth band,—that in the violet—stands apart and probably corresponds to a different electronic excitation state. This interpretation leads to the term system shown in Fig. 5.

TABLE I. Absorption bands of porphin.

λ(mμ)	613		560.5		517.5		487		430
ν(cm^{-1})	16300		17820		19300		20530		23260
$\Delta\nu$(cm^{-1})		1520		1480		1230		2730	

III

The change of color from purple to green, associated with the hydrogenation of one pyrrole nucleus in porphin—i.e., the conversion of a porphyrin to a chlorin—is caused by the appearance of a new, remarkably sharp and intense band in the red. This phenomenon is illustrated by Fig. 6[3] which shows the long wave part of the absorption curve of a chlorin superimposed upon the absorption curve of the corresponding porphyrin (chloroporphyrin-e_4-dimethylester, with a spectrum of the *etio* type). Two types of

---

[1] A. Stern and H. Wenderlein, Zeits. f. physik. Chemie **A176**, 81 (1936).

[2] A. Stern, H. Wenderlein, and H. Molvig, Zeits. f. physik. Chemie **A177**, 40 (9936).

[3] A. Stern and H. Wenderlein, Zeits. f. physik. Chemie **A174**, 81 (1935).

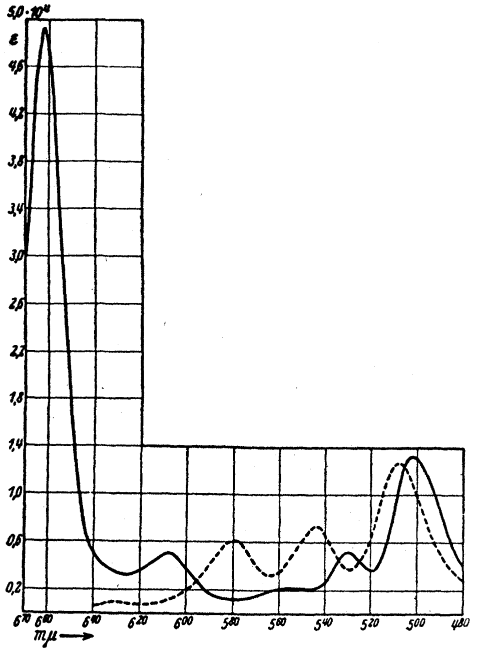

FIG. 6. Spectroscopic effect of hydrogenation of the porphin system (porphyrin-chlorin transition); ------ chloroporphyrin-e_4-dimethylester (in dioxane) and —— chlorin-e_4-dimethylester (in dioxane) (after Stern and Wenderlein, reference 3).

chlorin spectra—one characteristic of derivatives of chlorophyll *a*, and one of those of chlorophyll *b*—are illustrated by curves Nos. 4 and 5 in Fig. 3. The predominance of the red band over all the other bands in the visible region (except for the strong band in the violet, which is not much changed by hydrogenation) is particularly pronounced in curve No. 4 (*chlorin* type), but is recognizable also in the *rhodin* type (curve No. 5).

Figure 6 shows that simultaneously with the appearance of the strong red band, the bands in the yellow and green are weakened and displaced towards shorter waves. The position of the red band at about 660 mμ (i.e., considerably on the red side of the first band in Table I) and its predominant intensity indicate that it is due to a new electronic transition. The comparative strength of the band at 610 mμ in the hydrogenated compound makes it appear likely that ti too belongs to the new band system, as a second vibrational band, $X_0 \rightarrow Y_1$. It obscures the first band of the original four-band sequence, $X_0 \rightarrow A_0$, which was weak even before hydrogenation.

This interpretation leads to the term system shown in Fig. 7. It contains, in addition to the ground term X and the excited electronic terms A and B, "inherited" from the porphin spectrum, a new low excited term Y. The spectroscopic effect of the porphin-chlorin transition is shown in a different plot in Fig. 8.[4] This figure covers also the violet and ultraviolet, and shows that the violet band, too, is shifted by hydrogenation towards the shorter waves, but is not much changed in intensity.

IV

The interpretation of the red band group in chlorin as representing a new electron transition is supported by the analysis of the effect on the spectrum of the hydrogenation of the second "semi-isolated" double bond in the porphin system, i.e., the transformation of chlorophyll derivatives into bacteriochlorophyll derivatives. Figure 9 shows the absorption spectrum of bacteriochlorophyll itself.[5] It shows *three* main bands: one in violet (at about 400 mμ), one in the near red (at about 600 mμ), and a very prominent band in the near infra-red (at 780 mμ). Between the two bands in violet and red, one finds a pattern of weaker bands similar to that observed in porphins and chlorins. All these bands are weaker and situated further towards the shorter waves than the corresponding bands in

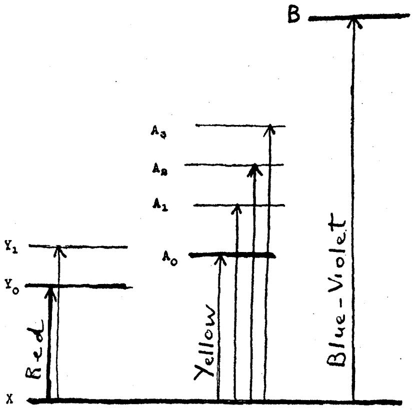

FIG. 7. Term system of a chlorin.

---

[4] A. Hagenbach, F. Auerbacher, and E. Wiedemann, Helv. Phys. Acta 9, 3 (1936).

[5] C. S. French, J. Gen. Physiol. 21, 71 (1937).

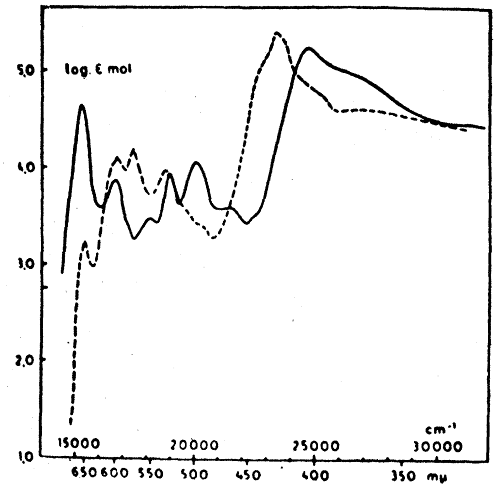

FIG. 8. Spectroscopic effect of a porphyrin-chlorin transition; – – – pheoporphyrin a_5 and —— dihydro pheophorbide (after Hagenbach, Auerbacher, and Wiedemann, reference 4).

chlorin spectra, not to speak of the spectra of the porphyrins. In short, the bacteriochlorophyll spectrum between 400 and 620 mμ appears as a chlorin spectrum with both the red and the yellow-green band system shifted towards the shorter waves and reduced in intensity. The infra-red band appears to be a new electronic band; its intensity overshadows that of the bands inherited from the chlorins even more strongly then the red chlorin band overshadows the yellow and green bands inherited from the porphyrins.

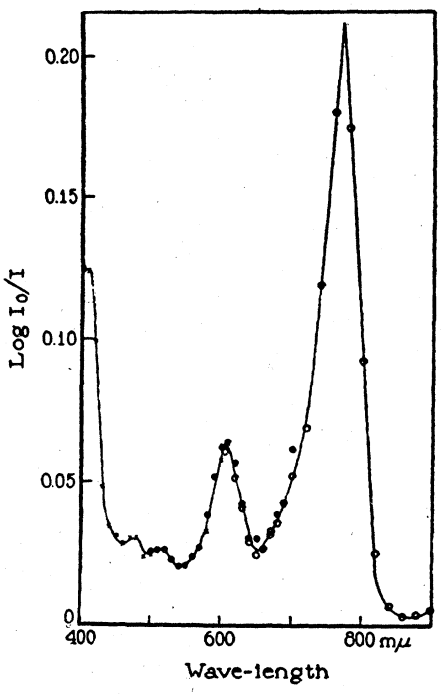

FIG. 9. Absorption spectrum of bacteriochlorophyll (in methanol (after French, reference 5).

According to this interpretation, the analogue of the red chlorophyll band in the spectrum of bacteriochlorophyll is the orange-red band at 600 mμ rather than the main red and infra-red band at 780 mμ.

The spectroscopic effect of the second hydrogenation step is thus a repetition of the effect of the first hydrogenation step—the appearance of a new low electronic excitation level. The transition to this new level assumes a preponderant probability; the previously lowest excited levels are shifted upwards, and the probability of transitions from the ground level to these "inherited" levels is reduced. The term system of tetrahydro porphin derivatives can

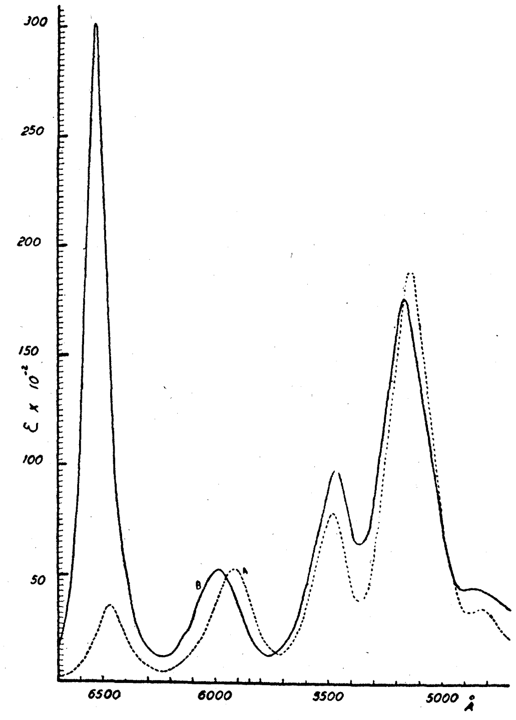

FIG. 10. Absorption curves of two tetraphenylporphin isomers (or of a tetraphenylporphin and a tetraphenylchlorin) (after Aronoff and Calvin, reference 6). (Fig. 1, J. Org. Chem. 8, 208 (1943).

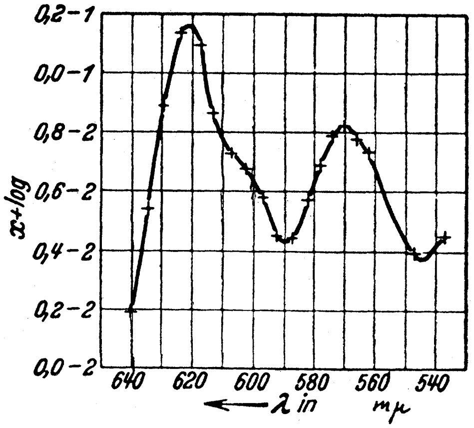

FIG. 11. Absorption spectrum of protochlorophyll *a* (after Rudolph, reference 9).

thus be derived from that shown in Fig. 7 by the addition of a new low level *Z* and by the upward shift of the levels belonging to the systems *Y* and *A*.

Aronoff and Calvin[6] synthesized what they thought at first were two isomers of tetraphenylporphin and found that while one of them had an *etio* type spectrum, the other one showed a typical chlorin band system (Fig. 10). Furthermore, they found that addition of hydrochloric acid to the alcoholic solution of the "isomer" with the porphyrin spectrum caused a gradual transition to the chlorin type. Here was a crucial test for the hypothesis that the strong red band is necessarily associated with the presence of two "extra" hydrogen atoms in one of the pyrrol nuclei. To maintain this hypothesis, one could suggest, for example,[7] that one phenyl group is linked not only to one of the bridge carbons (e.g., atom γ in Fig. 3) but also to a pyrrol nucleus, thus forming an additional ring (similar to the cyclopentanone ring in Fig. 3) and liberating two hydrogen atoms for the hydrogenation of another pyrrol nucleus. Calvin, Ball, and Aronoff[8] found in fact more recently that the two compounds belong to two different oxidation stages of the porphin system. Thus, the rule that the occurrence of the prominent red band is indicative of the dihydroporphin structure, appears to be correct in this case as well.

Some porphyrins are known which are green in color; the protochlorophyll (Fig. 3) is one example of this type. However, despite their color the spectra of these compounds are more like porphyrin spectra with a peculiar type of intensity distribution, than like true chlorin spectra. In the case of bacteriochlorophyll, for example, the 620 mμ band appears, both in its position and its intensity (relative to that of the bands in yellow and green), as an enhanced first vibrational band of the usual four-band sequence of porphyrins, rather than as an independent electronic band (cf. Fig. 11).[9]

V

The introduction of alkyl and carboxyl substituents, as well as of the vinyl group, the closure of the cylclopentanone ring, and the esterification of the carboxyls has little effect on the absorption spectrum of chlorin derivatives. (Cf. Fig. 12.) Two substituents in chlorophyll have considerable effect, if not on the general pattern of the spectrum, at least on the relative intensities of the individual bands. One is the central magnesium atom. The substitution of this metal atom for the two imido nitrogens present in porphin (cf. Fig. 1) causes an increase in the intensity of the main red band and a further weakening of the bands in the middle of the visible region. The result of this change is the beautiful pure green color of chlorophyll (as contrasted with the rather drab olive color of its magnesium-free derivative pheophytin). The absorption spectrum of the two chlorophylls *a* and *b* is reproduced in Fig. 13;[10] one sees that all the intermediate bands between the main red band and the main violet band have been reduced to relative insignificance by the combined effect of chlorin structure and magnesium.

VI

The difference between the absorption curves of chlorophyll *a* and chlorophyll *b* in Fig. 13

---

[6] S. Aronoff and M. Calvin, J. Org. Chem. **8**, 205 (1943).

[7] Cf. E. Rabinowitch, *Photosynthesis and Related Processes* (Interscience Publishers Inc., New York), Vol. II (in preparation), Chap. 21.

[8] M. Calvin, R. H. Ball and S. Aronoff, J. Am. Chem. Soc. **65**, 2259 (1943).

[9] H. Rudolph, Planta **21**, 104 (1933).

[10] F. P. Zscheile, and C. L. Comar, Botan. Gae. **102**, 463 (1941).

illustrates the effect of another substituent—carbonyl group in position 3—(shown by asterisk in Fig. 2). This group is the distinctive mark of all compounds of the chlorophyll *b* series. The red bands of these compounds are somewhat weaker and their other bands somewhat stronger than those of the corresponding compounds of the *a* series. Their spectra are of type 5 (*rhodin* type) in Fig. 3. It is noteworthy that the carboxyl group in position 3, where the C=O double bond is conjugated with one of the "semi-isolated" double bonds in the porphin system, has a much stronger effect on the spectrum than a similar group in position 9 where it is conjugated with the all-round "aromatic" ring system. (Cf. Fig. 2.)

VII

The spectroscopic properties of the porphyrins and their hydrogenated derivatives offer an interesting field for theoretical interpretation. The chromorphoric properties of the porphin system must be explained in the same way as those of the other "aromatic" systems. According to the resonance concept, one can visualize the actual structure of these systems as a result of superposition of two states of equal energy but different distribution of double and single bonds (as in the two Kekulé structures of benzene). The transition from one distribution to the other involves a shift of two electrons of each double bond to the neighboring single bond, i.e., a large displacement of electric charge in the molecule. Because of the equal contribution of the two distributions to the ground state, as well as to the low excitation state of the molecule, each of these states separately does not involve an oscillation of the electric charge in the molecule; but because of phase differences between the eigenfunctions of the two states, their co-existence (as envisaged in the quantum theory of light emission and absorption by atomic systems) leads to an electric dipole oscillation, whose intensity is of the same order of magnitude as that caused by a shift from one Kekulé structure to the other. This large dipole oscillation means large probability of light absorption or emission, i.e., the system is a strong chromophore. Because of the great length of the porphin ring (compared e.g., to the benzene ring) and the consequent

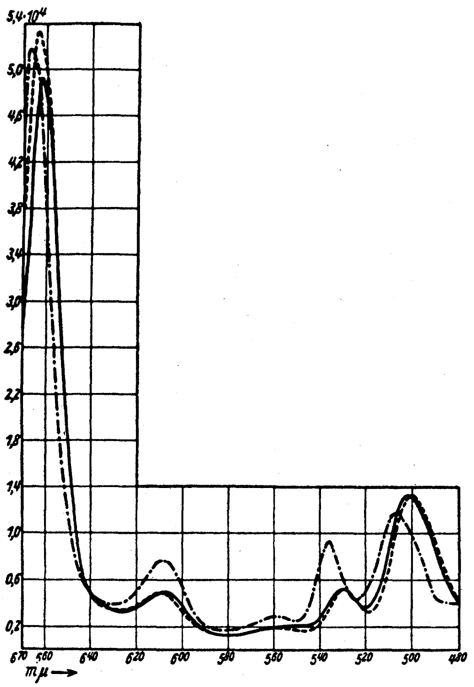

FIG. 12. Effect of closure of the cyclopentanone ring on the spectrum of a chlorin (1) —— chlorin-e_4-dimethylester (in dioxane) (2) ------ chlorin-e_6-trimethylester (in dioxane) (3) —·—·—· pyropheophorbide-*a*-monomethylester (in dioxane); (1) and (2) ring open, (3) ring closed (after Stern and Wenderlein, reference 3).

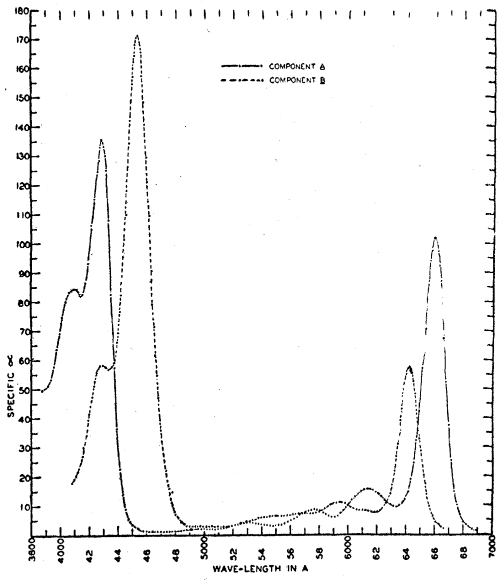

FIG. 13. Absorption spectra of chlorophylls *a* and *b* (in ether). (After Zscheile and Comar, reference 10).

multiplicity of excited states, the distance between the ground state and the lowest excited state is comparatively small, and the absorption bands are situated in the visible or infra-red, instead of far ultraviolet as in benzene.

The interesting problem in the interpretation of the spectra of porphin derivatives is the apparent successive addition of two new low electronic excitation states by the hydrogenation of porphin to dihydroporphin and tetrahydroporphin. It would be easier to explain an opposite effect, since the addition of new unsaturated groups provides new possibilities of resonance and could thus easily lead to the creation of new low excitation states; instead, low excited states *disappear* with increasing unsaturation!

VIII

Because of this apparent difficulty of interpretation, one may be inclined to attempt a different explanation of the origin of the red band of dihydroporphin and of the infra-red band of tetrahydroporphin. One could suggest, e.g., that they are low vibrational bands, which are merely too weak for observation in the spectra of porphin derivatives. In other words, one could suggest that the band sequence of porphin in Table I begins not with the $0\rightarrow0$ band, but with the $0\rightarrow2$ band. In dihydroporphin derivatives, the $0\rightarrow1$ band becomes the most probable transition, and in the tetrahydroporphin derivatives, the same occurs with the $0\rightarrow0$ band. The greater symmetry of the molecule, achieved by saturation of unsaturated side groups, may be suggested as an explanation of the decrease in the number of vibrations excited simultaneously with the excitation of the electronic system.

However, this explanation appears less adequate and more artificial than the assumption of new low electronic states. It has been observed[11] that the absorption bands of bacteriochlorophyll derivatives are about twice as strongly affected by variations in the nature of the solvent than are those of chlorophyll; the bands of chlorophyll are, in their turn, more sensitive to the influence of solvents than those of the porphyrins. The difference is more easily explained by the concept of different electronic excitation states than by the assumption of different vibrational levels. Low vibrational levels should be *less*, and not more sensitive to external electric fields than the higher ones, and should therefore suffer less displacement under the influence of different solvents. Molecules with lower electronic excitation states, on the other hand, have greater polarizability, and should therefore be more strongly affected by external electric fields, than molecules whose excited electronic states have a higher energy. Another argument in favor of the assumption of new electronic states will be derived below from the analysis of one fluorescence spectra of porphin derivatives of different degree of saturation.

IX

The relationship between the red or infra-red absorption bands and the presence of "extra" hydrogen atoms in the pigment molecule, is of interest in connection with the problem of the photochemical function of chlorophyll and bacteriochlorophyll in the photosynthesis of green plants and purple bacteria. The only excited states of pigment molecules which are of importance in the discussion of these photochemical reactions are the upper states of the red or infra-red absorption bands. This conclusion can be drawn from the comparison of the fluorescence spectra of these pigments with their absorption spectra. Most (although not all) derivatives of porphin, dihydroporphin, and tetrahydroporphin are fluorescent, and in all cases where the fluorescence spectrum has been investigated, it has been found to consist of a sequence of bands, rapidly declining in intensity towards the longer waves, with the most prominent band situated closely on the red side of the first absorption band. As an example, Fig. 14 shows the fluorescence spectrum of the two chlorophylls *a* and *b*. While the absorption band of chlorophyll *a* has a peak at 660 mμ and declines steeply towards the longer waves (cf. Fig. 13), the fluorescence band rises steeply at 650 mμ and reaches a peak at 665 mμ.[12] The fluorescence

---

[11] E. Katz and E. C. Wassink, Enzymologia **7**, 97 (1939); F. Pruckner, Zeits. f. physik. Chemie **A183**, 257 (1940).

[12] F. P. Zscheile and D. G. Harris, J. Phys. Chem. **47**, 623 (1943).

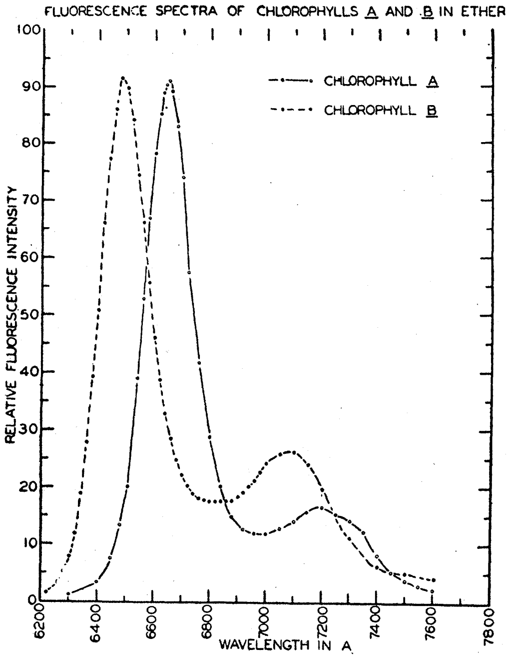

FIG. 14. Fluorescence spectra of chlorophylls *a* and *b* (after Zscheile and Harris, reference 11).

spectrum is independent of the color of the exciting light. It corresponds to transitions from the non-vibrating level Y_0 in the Fig. 7, to a sequence of vibrational levels of the ground state X. Table II shows the peaks of the three fluorescence bands of chlorophyll *a* and the vibrational quanta calculated from them.

The complete absence of fluorescence in the yellow, green, and blue-violet bands (even when ultraviolet light is used for excitation) shows that the lifetime of the excited states A and B is very short. Integration of the intensity of the blue-violet absorption band permits one to estimate (using the quantum mechanical relationship between transition probability and lifetime), the natural lifetime of the state B. It is about 3×10^{-8} sec. The absence of even 0.1 percent fluorescence in the violet band indicates that the actual lifetime of the state B is reduced, in organic solutions, to $<3\times10^{-11}$ sec. Since the yield of red fluorescence is approximately the same in blue and in red exciting light, the rapid dissipation of energy of the state B must be caused by a quantitative conversion to state Y which occurs within 10^{-11} sec. The same applies to state A. The vibrational quanta of state Y also are dissipated, before any fluorescent light is emitted, so that all fluorescence originates in the non-vibrating state Y_0. The intensity of the red absorption band indicates for this state a natural lifetime of about 8×10^{-8} sec.; if in solution, the fluorescence yield is of the order of 10 percent,[13] the actual mean lifetime of chlorophyll in the state Y_0 is of the order of 8×10^{-9} sec. Some observations indicate that the energy of this state, not used for fluorescence, is not converted directly into heat, but is first utilized for conversion of the pigment into a long-lived active form. Such an active product can be formed either by tautomerization of chlorophyll[14] or by a reversible reaction with the solvent.[15]

TABLE II. Fluorescence spectrum of chlorophyll *a*.

λ(mμ)	665[a]		7.20[a]		801[b]
ν(cm^{-1})	15040		13890		12435
Δν(cm^{-1})		1150		1455	

[a] See reference 12.
[b] A. Dhéré and A. Rappy, Bull. soc. chim. biol. **17**, 1385 (1935).

It is noteworthy, that the same relationship between absorption and fluorescence spectra, as described above for the case of chlorophyll and the chlorine, is observed also in the fluorescent derivatives of porphin and teatrahydroporphin An example is provided by the fluorescence spectrum of porphin itself,[16] whose band maxima are shown in Table III.

By far the strongest band is that at 616.5 mμ —just on the red side of the first absorption band (613 mμ, cf. Table I). The weak band at 591 mμ apparently is an "anti-Stokes" band, i.e., it originates in a vibrating level of the excited porphin molecule. The fact that the 613 mμ-band of porphin ($X_0 \rightarrow A_0$ in Fig. 5) is

---

[13] J. A. Prins, Nature **134**, 457 (1934).

[14] J. Franck and R. Livingston, J. Chem. Phys. **9**, 184 (1941).

[15] The suggestion that the long-lived active products formed by organic dyes in light may be the pigments in metastable (triplet) electronic states, made by G. N. Lewis and M. Kasha, J. Am. Chem. Soc. **66**, 2100 (1944), seems implausible [E. Rabinowitch, *Photosynthesis and Related Processes* (Interscience Publishers, Inc., New York, 1945), Vol. I, Chap. 18]. If these electronic states were stable enough to account for the observed phosphorescence and sensitization effects, the transition from the original excited state to these metastable states should be much too slow to compete effectively with fluorescence.

[16] A. Stern and M. Molvig, Zeits. f. physik. Chemie **A175**, 38 (1935).

TABLE III. Fluorescence bands of porphin.

$\lambda(m\mu)$	591		616.5		644		669.5		689
$\nu(cm^{-1})$	16900		16200		15500		14950		14600
$\Delta\nu(cm^{-1})$		700		700		550		350	

the weakest band in the absorption spectrum does not prevent it from giving rise to the strongest band in fluorescence. Apparently, porphin molecules, excited to the electronic state B or to one of the vibrational levels (A_1, A_2) of state A, rapidly lose all energy in excess of that of the state A_0. This dissipation is completed within $\ll 10^{-8}$ sec. The state A_0, which is the lowest excited state of porphin, survives, on the other hand, long enough to permit a considerable yield of fluorescence.

In tetrahydroporphin derivatives (e.g., bacteriochlorophyll) the main fluorescence band is associated with the absorption band in the red and infra-red. In this case, all electronic and vibrational excitation energy is excess of that of the lowest excited state Z_0 is lost by dissipation before any fluoresence is emitted.

The relationship between the first absorption band and the main fluorescence band in the derivatives of porphin, dihydroporphin, and tetrahydroporphin provides an additional—and perhaps decisive—argument for the attribution of the red and infra-red bands of the hydrogenated compounds to new electronic levels. If the alternative explanation suggested in VIII were correct, and the upper level of the red chlorophyll band, for example, were a low vibrational level of the electronic state A of the porphin system, then there would be no reason why the fluorescence of porphin should not originate from this low level. The main fluorescence band of porphin should then be situated at a considerable distance from the first absorption band of this compound (613 mμ) and close to the main fluorescence band of chlorophyll (655 mμ). By a similar reasoning, taking into consideration also the spectra of the tetrahydroporphin derivatives, one would expect the main fluorescence band of both the porphyrins and the chlorins to lie in the infra-red, in the neighborhood of the fluorescence band of bacteriochlorophyll. Since this is not the case, the states A_0 of the porphyrins, Y_0 of chlorins and Z_0 of bacteriochlorins must be independent vibration-free electronic states.

X

If one assumes that chlorophyll and bacteriochlorophyll participate in photosynthesis in the states Y_0 and Z_0, respectively, the relationship between these electronic states and the presence of extra hydrogen atoms in the pyrrole nuclei IV and II becomes important from the point of view of the possible role of these hydrogen atoms in the reduction of carbon dioxide. In the theory of photosynthesis, a sixty-year-old controversy between the "physical sensitization" theory, originated by Reinke, and the "photochemical catalysis" theory first formulated by Timiriazev, has not yet been resolved. According to the second concept, which is the more plausible of the two,[17] light-excited chlorophyll molecules act as intermediary oxidation-reduction catalysts, transferring hydrogen atoms to the oxidant (i.e., directly or indirectly, to carbon dioxide) and recovering them from the reductant (i.e., directly or indirectly, from water in green plants and from hydrogen sulfide or other inorganic or organic reductants in purple bacteria). Whether light energy is utilized only in the oxidation step (i.e., in the oxidation of chlorophyll and reduction of the reduction substrate) or only in the reduction step (i.e., reduction of oxidized chlorophyll and oxidation of the oxidation substrate), or in both steps, is an open question. Experiments *in vitro*[18,19] indicate that light-activated chlorophyll (in contrast to many other dyes which easily form leucodyes), has more tendency for oxidation than for reduction. This makes it plausible that *in vivo*, too, one (or the only) primary step in photosynthesis involves the photochemical oxidation (dehydrogenation) of chlorophyll.

The association between the excited states Y and Z of chlorophyll and bacteriochlorophyll and the presence of "extra" hydrogen atoms may mean that the excitation of these states activates

---

[17] E. Rabinowitch, *Photosynthesis and Related Processes* (Interscience Publishers, Inc., New York, 1945), Vol. I, Chap. 19.

[18] E. Rabinowitch and J. Weiss, Proc. Roy. Soc., London, **A162**, 251 (1937).

[19] J. Böhi, Helv. Chim. Acta **12**, 121 (1929).

these hydrogen atoms and makes them capable of reducing carbon dioxide (or an intermediate H-acceptor). This is a practically particularly important example of the as yet hardly investigated problem of specific activation by light of different atoms and groups in a complex molecule.

If the red absorption band were merely an additional vibrational band of the porphin band system, whose intensity is enhanced by the saturation of a non-saturated side group and consequent increase in molecular symmetry, then one would see no reason for a specific photochemical activation of the hydrogen atoms in this group. If, on the other hand, the upper level of the red band is a new electronic level associated with the presence of the two extra hydrogen atoms, then such a specific activation is not implausible. The solution of this problem appears to be of considerable importance for the understanding of the role of chlorophyll and bacteriochlorophyll in photosynthesis.