

Spectra of Porphyrins*

MARTIN GOUTERMAN

Conant Chemical Laboratory, Harvard University, Cambridge, Massachusetts

The review opens by presenting the absorption spectra for three series of porphyrins derived from the basic skeleton: (a) compounds obtained by simple substitution; (b) compounds obtained by reduction of one or more pyrrole rings; and (c) compounds obtained from fusion of aromatic rings onto the basic skeleton. The spectra are discussed in terms of a four orbital model—that is intensity changes and energy shifts are related to the properties of two top filled and two lowest empty pi orbitals. Emission spectra of metal porphyrins are then discussed, three metal series being distinguished: (1) In closed shell metals, the continuous enhancement of phosphorescence at the expense of fluorescence is attributed to spin-orbit coupling. (2) In paramagnetic metals, observed effects are attributed to the existence of a state at the same energy as the usual triplet but with multiplicity the same as the ground state; its intensity is ascribed to exchange interactions. (3) In diamagnetic metals with unfilled *d* shells, peculiar emission properties are attributed to enhanced spin orbit coupling due to low lying metal triplets. The review closes by discussing *n-π* transitions and triplet-triplet spectra.

I. INTRODUCTION

The porphyrins have long been important in biology because of their central role in photosynthesis, biological oxidation and reduction, and oxygen transport. However, the spectra of these molecules may be expected to become increasingly important in chemical physics. This increase in importance stems from the extensive development of the past decade of theory and experiment on the spectra of aromatic hydrocarbons. The porphyrins present a large cohesive set of spectra on molecules that are aromatic yet with the extra complexity of nitrogen atoms. It is therefore natural to look to them as a logical ground for the generalization of current theory. We shall review porphyrin spectra from this point of view of chemical physics and refer the reader to other reviews that more directly relate the porphyrin spectra to biological function (1, 2). The fact that both theoretical chemistry and biology are converging on these molecules gives these studies some added excitement.

As we shall show, a firmly established theory for the porphyrin spectra is not at hand. However, since considerable progress has been made, we shall present

* This work was supported by a grant from the National Institutes of Public Health.

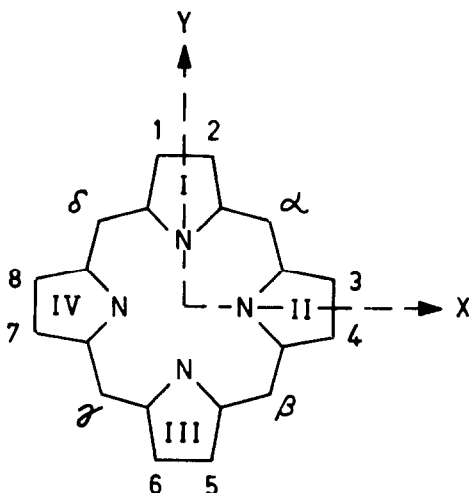


FIG. 1. Basic porphyrin skeleton

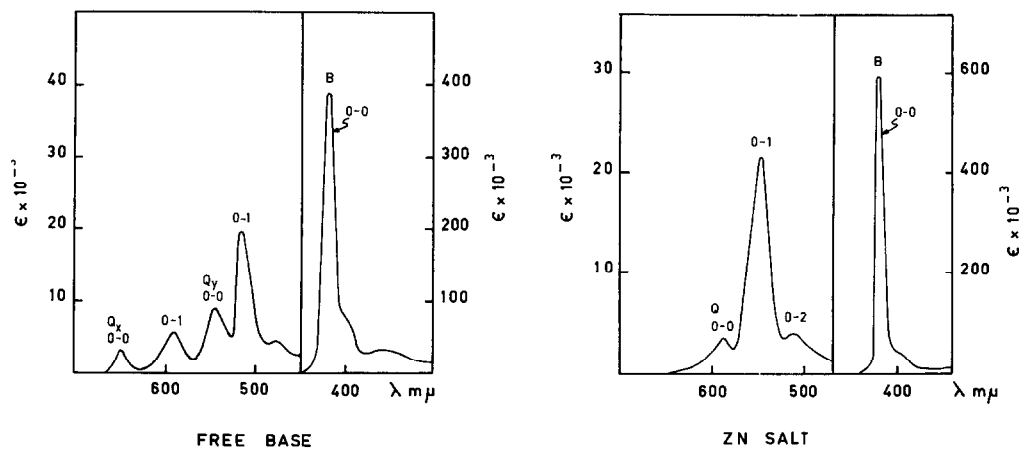
the theory in a logical rather than in an historical development. It is hoped that this presentation will make the review more readable and more stimulating. However, it has necessitated a reformulation of past work in slightly new terms as well as an extension to material never fully treated. Moreover, a logical development necessarily sacrifices extensive summaries of previous theoretical treatments.

This review will also attempt to point out areas for future research. By this we definitely admit that the present formulation is not final. However, as in a similar review by Rabinowitch (3) some years ago, we hope this present resumé will serve as a convenient starting point for future developments.

II. ORGANIZATION

Figure 1 shows the basic porphyrin skeleton with the rings and positions labeled and with axes chosen. If at each position 1 through 8 and α through δ there is a single H atom and two H atoms in the center, the compound is called *free base porphin*. The outer H atoms can be substituted as in benzene; the molecules so derived are referred to as *porphins*. Another type of substitution replaces the central H atoms by any one of a variety of metals, thus changing from a free base to the metal salt. A second series of porphyrins, no longer called porphins, arise by reducing the outer bonds 1—2, 3—4, etc. One, two, and three such reductions are reported. Finally a third series of porphyrins arise by fusing benzene rings across the outer bonds 1—2, 3—4, etc. These latter two series can also be substituted at the external positions and can exist as either free base or metal salt.

Our review will begin by discussing the absorption spectra of the three series



FREE BASE
ZN SALT
FIG. 2. Absorption spectra of tetraphenyl porphin (Ref. 4)

defined above: porphins, reduced porphins, and benzporphins. From this we go on to emission spectra, which we will discuss for all porphyrins.

All the spectra of the first discussions are presumed to be singlet-singlet or triplet-singlet π - π transitions. In addition to these, n - π transitions can arise in C=O substituted porphyrins. Moreover, with suitable techniques a triplet-triplet spectrum can be obtained. We will close the review by discussing these latter two more exotic spectral phenomena.

III. ABSORPTION SPECTRA OF PORPHINS

A. EXPERIMENTAL FACTS

Figure 2 shows a typical spectrum of a free base porphin, $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin (4). All free base porphins show a similar four-banded visible spectrum of moderate intensity in the region 6600 Å to 5000 Å and an extremely strong band, called the Soret band, at 4000 Å. Tetraphenylporphin is an artificial compound. The naturally derived compounds have alkyl, vinyl, or carbonyl groups on positions 1 to 8 and, occasionally, a methine bridge substituent or a C—C bridge from positions 6 to γ .

In a series of papers Stern and coworkers (5) reported the visible spectra of some 40 such porphins. He empirically classified the spectra into the three types (6) shown in Fig. 3. Thus the experimental facts on free base porphins may be summarized as a spectrum like that of Fig. 2, with the visible bands varying as in Fig. 3. A more severe substitution is that of aza-nitrogen replacing a methine bridge. This substituent greatly increases the intensity of the visible bands (7).

A more striking spectral change occurs when a free base is converted to a metal salt. The spectrum of Zn tetraphenyl porphin shown in Fig. 2 exhibits the effect, the four-banded visible spectrum collapses into two. If the metal is changed

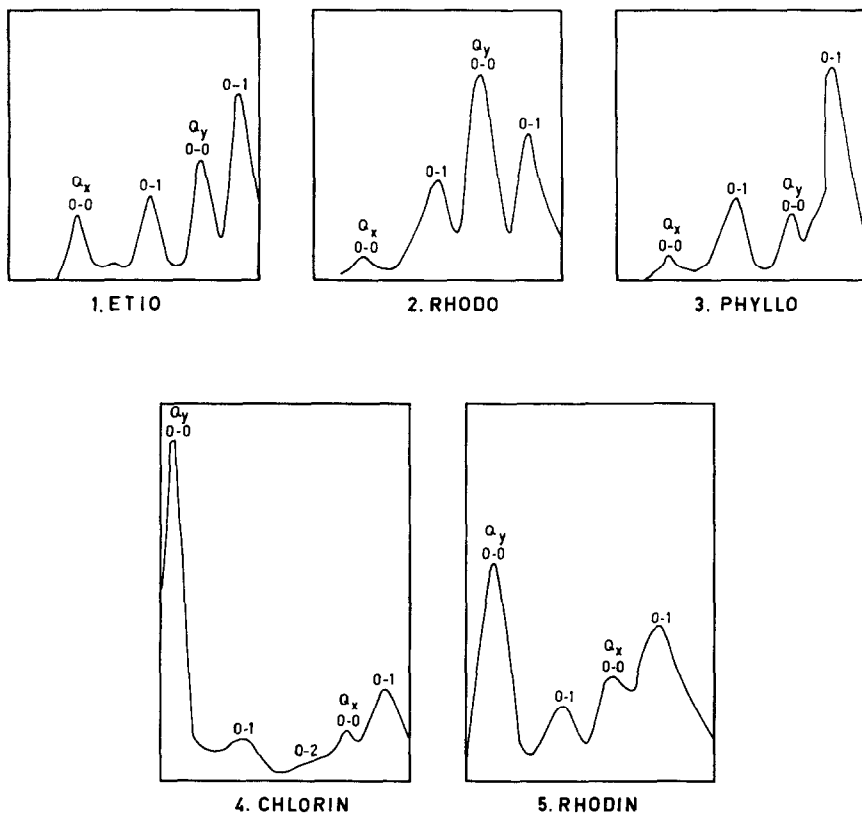


FIG. 3. Porphin visible band types: etio, rhodo, phyllo. Chlorin visible band types: chlorin and rhodin (Ref. 6).

in a given porphin skeleton, the spectrum changes in two ways: the intensity of the long wavelength band varies and the whole spectrum shifts in wavelength (4, 8).

B. INTERPRETATION

We shall interpret the experimental facts given above by what might be called a four orbital model. This is a somewhat new way to express the theory. It has been adopted because it naturally extends itself to the reduced porphins and also because it seems to have considerable intuitive appeal. This new form of the theory should not obscure the fact that most of the ideas have been previously developed. Simpson (9) first related porphin to the 18-membered cyclic polyene; Longuet-Higgins *et al.* (10) gave the first MO treatment of porphin; Platt (11) first attempted to explain substituent effects with his vector model, which the author (12) later investigated in considerable detail. The present formulation

also draws heavily from the theory of alternant hydrocarbons (13), with considerable inspiration from the Moffitt (14) theory of cyclic polyenes and the Pariser and Parr (15) and Ham and Ruedenberg (16) treatments of configuration interaction in aromatic hydrocarbons.

Before discussing the model it is useful to present the nomenclature. The visible bands are ascribed to π - π transitions (9-12). For a metal porphin, with D_{4h} symmetry, such transitions are of E_u symmetry; that is they consist of two equivalent dipole transitions in the x and y directions. In the metal porphin spectrum shown in Fig. 2, we have labeled the visible bands Q and the uv bands B ; we use the names to refer to both the bands and the pairs of excited states of the transitions (11, 12). Certain bands of the spectra have been classified as vibrational peaks on the basis of the constancy of their energy separation from the 0-0 peak and their relatively constant intensity (11). We use the labels Q_x , Q_y , B_x , B_y for the individual components of the transition pairs. In the free base, the x and y axes are no longer equivalent, and so the splitting of the Q_x and Q_y bands, shown in Fig. 2, should therefore not be surprising. However, the full meaning of this behavior will be clarified in the ensuing discussion.

We begin by considering a cyclic polyene of 4ν or $4\nu + 2$ CH-groups. Such systems are of symmetry species $D_{4\nu,h}$ or $D_{4\nu+2,h}$. The orbitals giving rise to the electronic transitions will be of symmetry species e_ν and $e_{\nu+1}$ (14). These are two pairs of degenerate orbitals (Fig. 4A) with ν and $\nu + 1$ nodes, respectively. In polyenes $4\nu + 2$, the orbitals e_ν are filled. Transitions $e_\nu \rightarrow e_{\nu+1}$ give rise to the singlet states E_{1u} , B_{1u} , and B_{2u} , as shown in Fig. 4B; the latter two states are forbidden (14). A 4ν polyene will have e_ν only half filled. However, if we assume the e_ν orbitals are somehow filled, group theoretical arguments show that the symmetry of the singlet states arising from these same transitions will be E_{1u} and $E_{2\nu-1,u}$. The latter pair are still forbidden but are now degenerate, as is also shown in Fig. 4B.

This difference in the behavior of the forbidden bands is very important for an understanding of porphin spectra. Whether the forbidden bands are necessarily degenerate is determined by group theory. However, the cause of the splitting is not a change in the orbital energies. The cause has been shown to be electronic interaction terms (16). This distinction will prove significant to the porphins.

To relate such considerations to the porphin molecule, we need to know the top filled and lowest empty orbitals of porphin. These are shown in Fig. 5 as obtained from naive MO calculations (10). The top filled orbitals have symmetry a_{2u} and a_{1u} . We shall refer to them as b_1 and b_2 (16), for the symmetry labels become inappropriate in porphyrins of lower symmetry. The lowest empty orbitals have symmetry e_g , referred to as c_1 and c_2 . The figure shows that b_1 and b_2 have 4 nodes, c_1 and c_2 have 5 nodes, if one counts the nonsymmetry

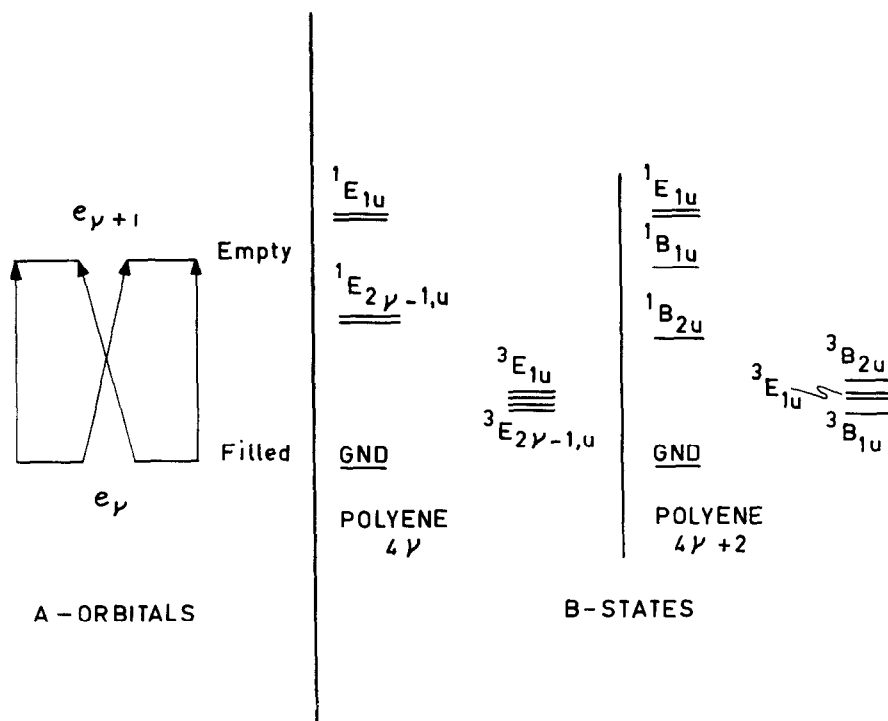


Fig. 4. Orbitals and states of cyclic polyenes

nodes also. Thus they resemble the orbitals e_4 and e_5 of a 16- or 18-membered cyclic polyene.¹

There is one important difference between porphyrin orbitals of MO theory and cyclic polyene MO's. The orbital b_1 is calculated to have much higher energy than b_2 . Thus MO treatments have identified the visible bands with transition $b_1 \rightarrow c_1, c_2$ and the Soret band with $b_2 \rightarrow c_1, c_2$ (10, 17-19). This identification requires both bands to be of equal intensity. It thus fails to account for the radical difference in intensity of the visible and w systems, shown in Fig. 2. To account for this intensity difference it is necessary to assume that, contrary to the naive MO calculations, the top filled orbitals are accidentally degenerate. This makes the cyclic polyene model applicable and transitions to the visible bands forbidden (11, 12).

Let us apply these considerations to the spectra of the metal tetraphenylporphyrins. Because the transitions must occur in degenerate pairs, the states

¹ The significance of a 16-membered polyene has been stressed by G. R. Seely (private communication).

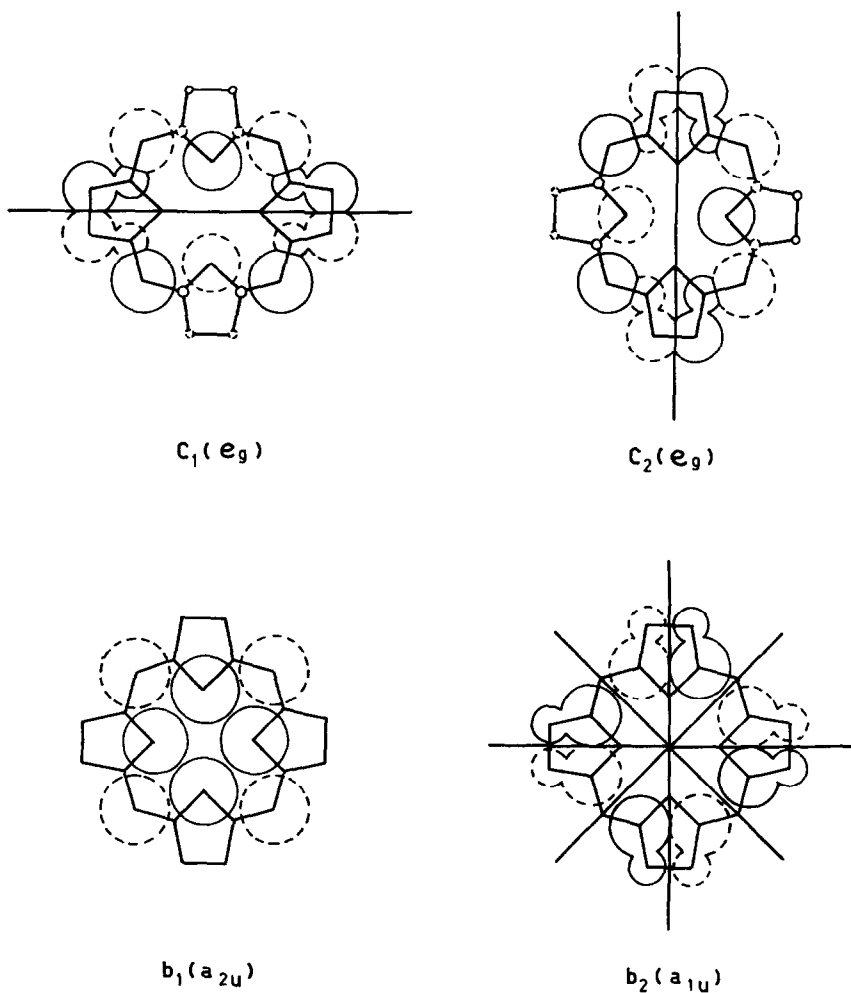


FIG. 5. Porphin MO's. The atomic orbital coefficients are proportional to the size of the circles; solid or dashed circles indicate sign. Symmetry nodes are drawn in heavy lines (Ref. 10).

must be like those of the 16-membered cyclic polyene. An excellent agreement with the experimental spectra is obtained if it is assumed that the main effect of the metal on these transitions is the conjugation of its p_x orbital with the π electrons of the ring (12). Because of the nodal properties, shown in Fig. 5, this orbital can only interact with the a_{2u} orbital. It has been shown that as the metal becomes more electropositive, this orbital rises in energy. In rising from the degenerate case, there will be two consequences: (1) the spectrum will shift to the red and (2) the visible band will intensify. The latter effect may be seen intuitively.

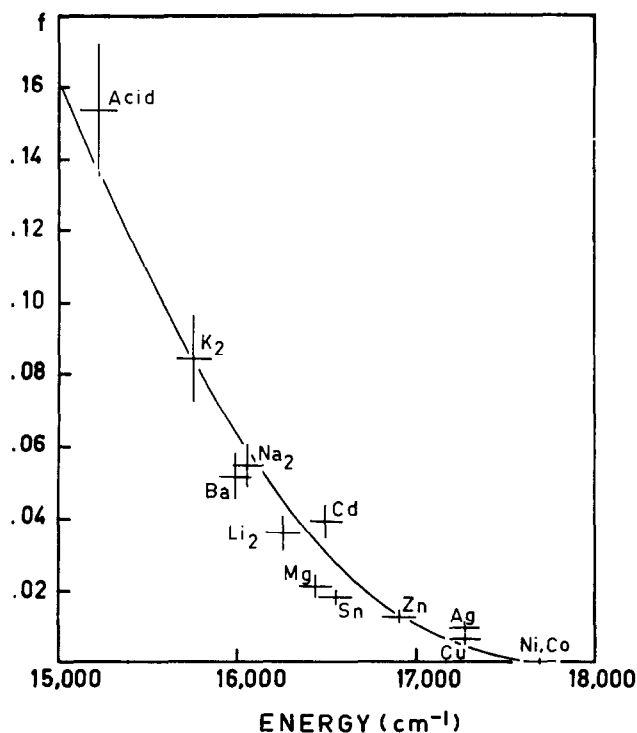


FIG. 6. Oscillator strength versus energy of $Q(0-0)$ band in metal tetraphenylporphyrins. Line is theoretical (Ref. 12).

tively, for in the limit that b_1 and b_2 differ widely in energy one returns to the naive MO prediction of a visible and uv band of nearly equal intensity. These ideas have been made quantitative (12). In Fig. 6 we show the agreement of experiment with the theoretical relation between intensity and energy in the lowest visible band of tetraphenylporphyrin.

The theory also interprets the change in the porphyrin spectra in going from the metal salt to the free base. Figure 7 shows how the opposite protons stabilize an eighteen-membered ring. (Adjacent protons have a similar effect. However, theoretical arguments have shown that adjacent protons are incompatible with the observed spectral changes (12).) This stabilization causes the excited states to become more like those of the 18-membered rather than the 16-membered polyene. Thus the visible bands Q_x and Q_y split (12).

Confirmation of the theory has come from two nice experiments. Weigl (20), in a fluorescence depolarization experiment, showed that the Q_x band is polarized perpendicularly to Q_y in agreement with the theory. Rimington *et al.* (21), in very pure free base porphyrin and low temperature, found a slight (250-cm)

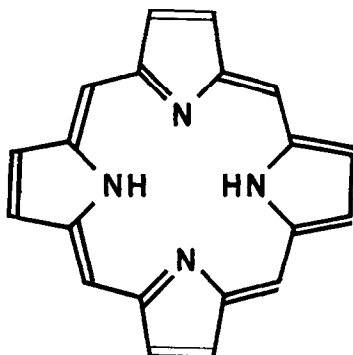


FIG. 7. Heavy bonds show 18-membered cyclic ring stabilized by the central H atoms

split in the Soret band, as is expected because of the presence of a B_x and B_y band. The cyclic polyene model also, predicts the band polarizations with respect to the H H axis. If the H H axis is in the x direction, as in Fig. 8, the Q_x band is the lowest as shown in Fig. 2. Although there is as yet no direct evidence for this, later we shall give an independent, though indirect, argument from the spectra that confirms this idea.

We shall now consider the effect of substituents on the free base spectrum. Figure 8 shows two cases of orbital energy splittings and polarizations of the porphyrin transitions. We shall refer the Q and B states of any arbitrary porphyrin to the following states Q^0 and B^0 :

$$\left. \begin{array}{l} B_x^0 \\ Q_x^0 \end{array} \right\} = [(b_1 c_2) \mp (b_2 c_1)]/\sqrt{2}$$

$$\left. \begin{array}{l} B_y^0 \\ Q_y^0 \end{array} \right\} = [(b_1 c_1) \pm (b_2 c_2)]/\sqrt{2}$$
(1)

where we use the symbols $(b_1 c_2)$ to denote singlet states for the transition $b_1 \rightarrow c_2$, etc. These states would arise if b_1 , b_2 and c_1 , c_2 were degenerate. The states B^0 give allowed uv bands and Q^0 forbidden visible. If it is assumed that states of different polarization will not mix, it may be shown by perturbation theory that the Q states of an arbitrary porphyrin are ($1\mathcal{Z}$):

$$Q_x = Q_x^0 + \lambda_x B_x^0$$

$$Q_y = Q_y^0 + \lambda_y B_y^0,$$
(2)

$$\lambda_x = \{(\epsilon(c_2) - \epsilon(b_1)) - [\epsilon(c_1) - \epsilon(b_2)]\}/2\Delta$$

$$\lambda_y = \{[\epsilon(c_1) - \epsilon(b_1)] - [\epsilon(c_2) - \epsilon(b_2)]\}/2\Delta,$$
(3)

where Δ is the initial energy gap between the allowed and forbidden bands and $\epsilon(b_1)$ is the orbital energy of b_1 , etc. The intensities of these Q states will be

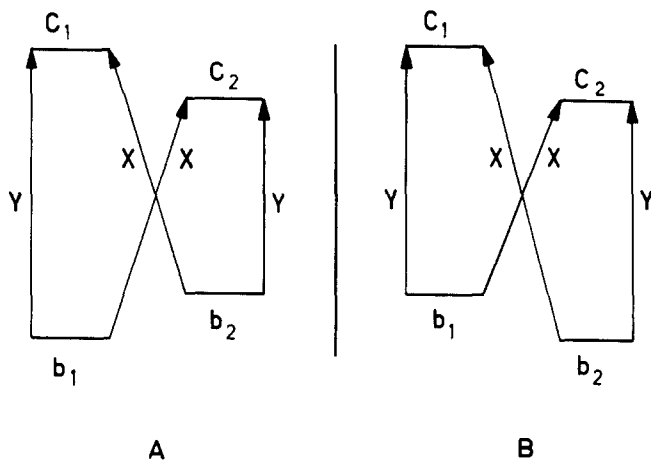


FIG. 8. Possible relations among the orbitals of porphyrin. HH axis is taken in x direction.

proportional to λ_x^2 and λ_y^2 , respectively. It may be seen that, for each polarization, as the equality of the transition energies breaks down the visible band becomes allowed.

Let us consider now the effect of free base formation on the orbital energies. Orbital c_1 has electron density on the nitrogens of rings I and III, while c_2 on nitrogens of II and IV. Since we place the protons on the latter two rings, we lower $\epsilon(c_2)$ with respect to $\epsilon(c_1)$. However, we cannot establish whether b_1 is higher or lower than b_2 . In Fig. 8A with b_2 higher, the x polarized transitions have nearly equal energy while the y pair differ. Thus Q_x is weak and Q_y strong. In Fig. 8B, with b_1 higher, the reverse is true.

A spectral argument can now be given to show that b_1 is actually lower in porphyrin itself. As one goes from porphyrin to octa-alkylporphyrin the intensity of the two Q bands rises continuously. Since this substitution is symmetric, it does not affect the splitting of the c orbitals; it can, however, split the b orbitals. As can be seen from the MO coefficients of Fig. 5, b_2 is affected but not b_1 . Since alkyl groups are electron donating, this substitution should raise b_2 with respect to b_1 . It can be seen that if b_2 were initially below b_1 , this would cause the intensity of the strong transition to decrease and the weak one to increase. However, if b_2 were initially above b_1 , then both Q bands would increase. Experimentally porphyrin shows a phyllo spectrum and octa-alkylporphyrin an etio spectrum. From this we conclude that in porphyrin b_2 is higher than b_1 and the lower band is polarized parallel to the HH axis, in agreement with the cyclic polyene model.

Similar arguments can relate the HH axis to axes set up by external substituents. Thus consider 1,2,5,6 tetra-alkylporphyrin versus 3,4,7,8. (Note we keep the HH axis in the X direction.) The MO coefficients of c_1 and c_2 are such that

in the 1,2,5,6 case c_2 is raised; for 3,4,7,8-tetra-alkyl c_1 is raised. The former effect tends to reduce the intensity difference of the two Q bands while the latter raises it. Since, in fact, this compound shows a rhodo spectrum, i.e., a heightened intensity difference, the H H axis and methyl axis must be parallel.

These types of arguments can rationalize the spectra in other cases. Thus a 6 CO substituent, being electron attracting, must lower both b_2 and c_2 from the etio values. This does not affect strong band but weakens weak ones giving the rhodospectrum. A γ -methyl substituent by raising the orbital b_1 closes the gap between b_1 and b_2 while not affecting that between c_1 and c_2 . We thus go back to a phyllo spectrum.

Additional confirmation of these ideas has been obtained from energy shifts of the bands. It can be shown that on increasing intensity of, say, the Q_x band, the Q_x and B_x bands should separate. Thus the energy gap between Q_x and Q_y should vary with their intensity difference. This has been found. However, other energy shift predictions have not worked out so nicely (12). Finally a last confirmation has been found in the aza-porphins, whose strong intensity and energy shifts can be explained with the same theory.

This model could be easily formulated into a vector theory like that of Platt (11). The vectors for each band would be all parallel. The author found some success with this for simple alkyl and carbonyl derivatives. The quantitative accuracy quickly breaks down with γ methyl and CO substituents. It has been pointed out (22) that γ methyl certainly forces a 6 CO out of the plane. Thus, substituent effects are not mutually independent. Moreover, undoubtedly with some substituents there is a mixing of Q_x with B_y , a possibility our theory omits. It therefore does not seem valuable to try to give a quantitative basis to this treatment. It is nonetheless hoped that its intuitive simplicity may be helpful in understanding spectral changes.

C. FUTURE WORK

The outstanding problem raised by this treatment is finding out as to what must be done with MO theory to obtain the required near degeneracy of b_1 and b_2 . Perhaps an extension of the Goodman and Harrell (23) treatment of nitrogen heterocycles may be the best approach. Another might be the S.C.F. treatment of Kobayashi (24). The latter requires the calculation of electronic interaction integrals that determine the splitting of the Q and B bands. Such integrals must also determine the intensely subtle cyclic polyene perturbation.

IV. ABSORPTION SPECTRA OF REDUCED PORPHINS

A. EXPERIMENTAL FACTS

Compounds with one double bond hydrogenated (which we take as 7-8) are called chlorins. Figure 9 shows their outstanding characteristic an intense red band (25). It also shows that, unlike the porphins, the change from free base to

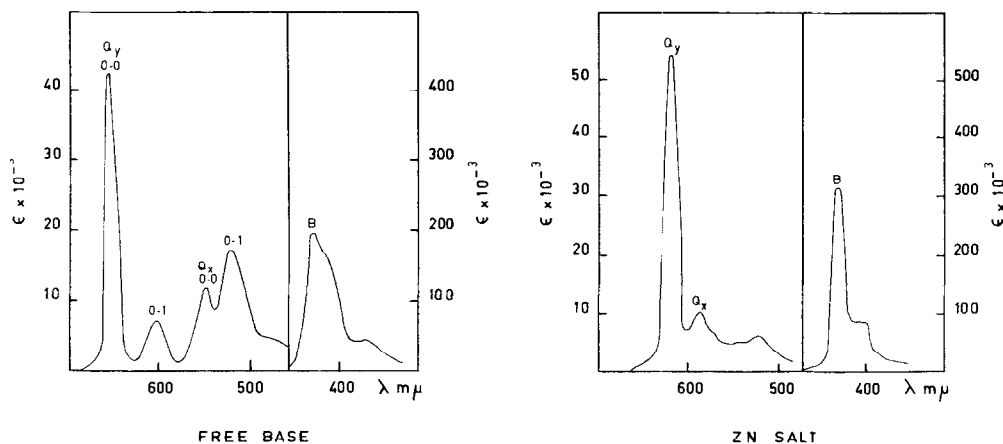


FIG. 9. Absorption spectra of tetraphenylchlorin (Ref. 25)

metal salt produces no great simplification of the visible bands. In Fig. 9 the bands are labeled. The rationale for choosing certain peaks as vibrational overtones is the same as for the porphins. Again we shall rationalize the labeling of electronic transitions in our later discussion.

The effect of substituents is less easy to characterize in chlorins. Stern proposed the chlorin and rhodin classification shown in Fig. 3. The latter type arises when a carboxyl group replaces an alkyl at position 3. The effect of other substitutions is less striking.

Compounds with two reduced rings are the tetrahydroporphins (THP). The reduced ring can be either opposite (OPPTH) or adjacent (ADJTHP) (19). The former is the same as the natural bacteriochlorins. Figure 10 shows the spectra of these two cases. Hexahydroporphin has also been reported (19).

B. INTERPRETATION

We shall extend the model developed above to these systems. This agrees with Platt (11) in treating reduction as a perturbation. However, the discussion derives mainly from the work of Seely (19), who was the first to consider all the compounds systematically.

Seely proceeded by calculating the MO's for the various reduced porphins. In all calculations he found two top filled orbitals and two lowest empty. These he showed to be descendents of the initial porphin orbitals b_1 , b_2 , c_1 , and c_2 . He then identified observed bands with various transitions among these orbitals. We shall accept Seely's MO calculations and assume that the orbitals of interest are descendents of the four orbitals of porphin. We assume, however, that Seely's orbital energies must be adjusted to make b_1 and b_2 degenerate in porphin. In this way we can find an amount of energy to subtract from b_1 and to add to

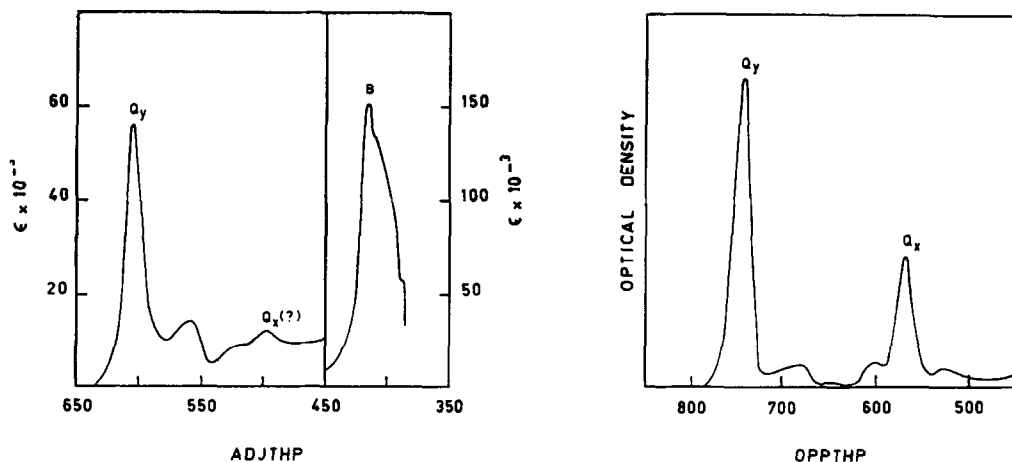


FIG. 10. Absorption spectra of tetrahydroporphins (Ref. 19)

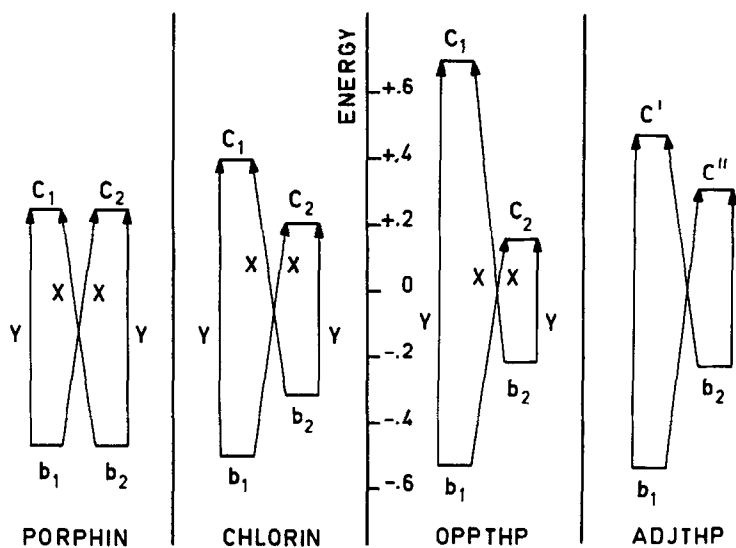


FIG. 11. MO levels in porphin, chlorin, OPPTHp, ADJTHp

b_2 to bring this about. We shall add and subtract this amount from b_1 and b_2 for chlorin and THP. In Fig. 11 we show the resultant MO energy levels.

The reason for the shifts in the MO energies can be understood quite well qualitatively. We have assumed that ring IV is reduced. This removes positions 7 and 8 from conjugation. Orbitals b_1 and c_2 have little electron density there and are not greatly affected. However, b_2 and c_1 do have electron density. Thus reduction acts to decrease their free electron box and so raises their energies.

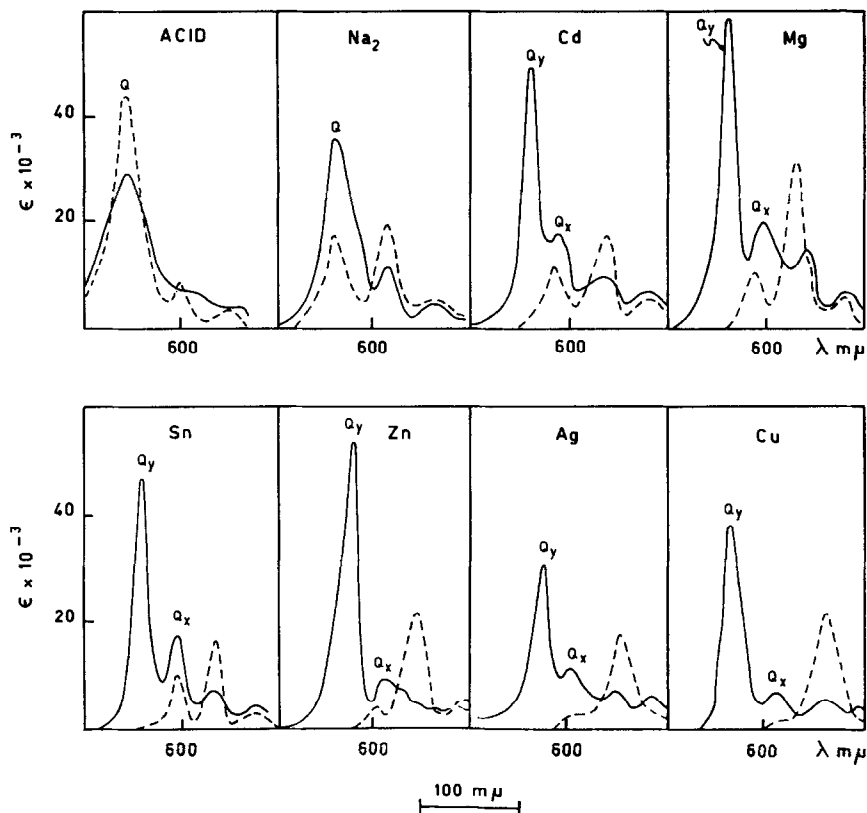


FIG. 12. Visible bands of tetraphenyl porphyrin and chlorin (Refs. 4 and 25). Chlorins are shown as solid line; porphyrins as dashed.

Consider now the chlorin orbitals. The x polarized transitions are nearly degenerate. These will combine, as in porphyrin, to give a weak visible and strong uv band. The y polarized transitions differ greatly in energy. It can be shown (12) that in such cases the resultant y polarized bands will be much more widely split than the x polarized pair and the intensity of the visible band will be strong. This accounts for our labeling of the bands in Figs. 3 and 9.

Some confirmation of the theory can be obtained from the metal chlorins. One might expect that, as in the porphyrins, the orbital b_1 rises with increasingly electropositive metals. In such a case, it is clear from Fig. 11 that the difference in behavior of the bands of two polarizations should tend to diminish as the energy split of b_1 and b_2 decreases. Figure 12 shows some metal porphyrin and chlorin visible bands. If we identify the chlorin Q_x band from its coincidence with the porphyrin Q bands, then indeed the Q_x and Q_y bands coalesce with increasingly electropositive metals. (We treat acid form as a metal as in Ref. 12.)

This theory predicts band polarizations. No experiments are reported on simple metal chlorins. However, the expected behavior has been reported for chlorophyll (26).

An important question is the effect of free base formation on the spectra. By choosing ring IV to be reduced, the resonance structures show we have forced the H H axis to be parallel to the y axis (contrary to our porphin convention). The cyclic polyene perturbation therefore lowers the energy of Q_y and raises Q_x , increasing their separation over that of the metal, as is observed in Fig. 9.

The theory also rationalizes chlorin and rhodin spectra. Qualitatively a CO group on ring II would lower c_1 and b_2 . It thus tends to reduce the energy and intensity difference of the Q_x and Q_y bands, the effect observed. Unfortunately, such explanations do not seem to work well for substitutions on other positions, as they predict more changes than are observed. It may be that after removal of ring IV, ring III becomes more sensitive, and there is some indication of this from Seely's calculations. Thus substituent theory here is not so well settled as for porphins.

Figure 11 also shows the adjusted energy levels of the two THP's. It is seen that in ADJTHP the two x polarized transitions are more nearly equal in energy than in OPPTH. We thus expect a more strongly allowed Q_x band in the latter, in agreement with experiments. (Since x and y are not symmetry axes in ADJTHP, band polarizations will be rotated 45° .) Although our arbitrary adjustment procedure is not very satisfactory theoretically, it can be seen that it does give a basis for understanding the differences between the spectra of the molecules.

C. FUTURE WORK

Theoretical treatment of the reduced porphins clearly waits on prior treatment of porphin. However, the basic interpretation of the spectra predicts polarizations of transitions, something that can be checked experimentally.

V. ABSORPTION SPECTRA OF THE BENZPORPHYRINS

Benzporphyrins have been synthesized and their spectra recorded by Linstead and coworkers (27). Tetrabutetrazabenzporphin, or *phthalocyanine*, is the most important; tetrabutetrazabenzporphin has also been made as well as tribenz and monobenz (28, 29). Almost no theoretical work has been done on these systems. We shall therefore confine our discussion to reproducing some of the spectra,² so as to show that the mechanisms proposed for porphin operate here.

Figure 13 shows the free base and Zn salt of tetrabutetrazabenzporphin. The cyclic polyene effect is still apparent. The visible bands are split by 1350 cm and the uv by 800 cm. The fact that there is a large uv band splitting can be related to

² The author wishes to thank Dr. Linstead and his coworkers for copies of their spectra and for the privilege of publishing here some not previously published elsewhere.

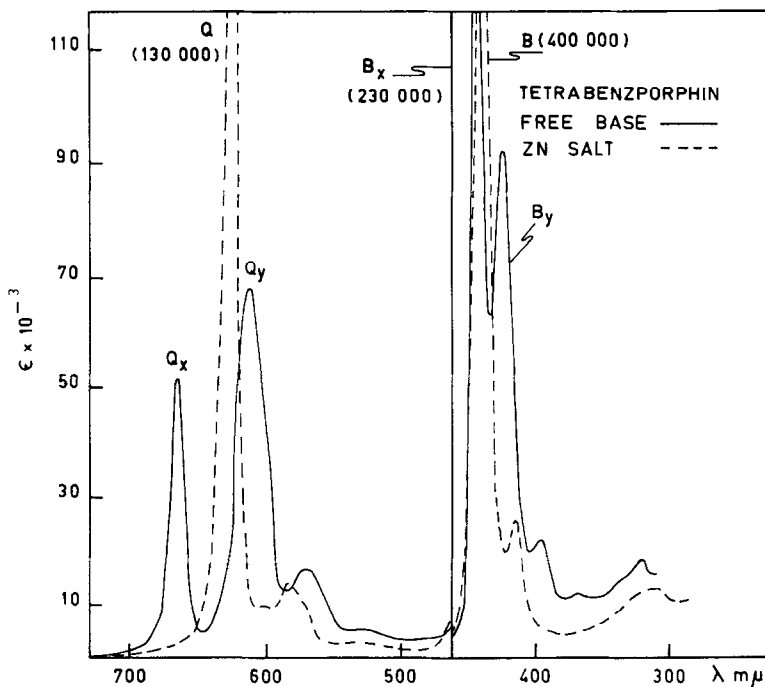


FIG. 13. Absorption spectra of tetrabenzporphyrin. (Linstead and coworkers, previously unpublished). Solvents: Free base—chloronaphthalene; Zn-pyridine.

the strength of the visible bands. Since the Q bands are so strong, it follows that the Q and B states are here extensive mixtures of the initial Q^0 and B^0 states. Thus the cyclic polyene splitting, which was confined to Q_0 , appears in both bands. Some simple mathematical consideration of this problem shows that (HH axis parallel X axis) the B_y band is the highest as indicated on the figure, a prediction that can be verified experimentally.

Figure 14 shows phthalocyanine free base and Zn salt. The splitting of the visible bands of the free base is still evident. The uv band, however, has a curious appearance; moreover, it seems much weaker than the visible bands. It can be shown that our model requires that the uv bands be stronger (12). However, a truer measure of intensity is dipole strength, which is given by (12):

$$q^2 = \frac{1}{2500} \epsilon \frac{\Delta\lambda}{\lambda},$$

where q^2 is dipole strength in square angstroms, λ is wavelength, $\Delta\lambda$ is halfwidth, and ϵ is molar extinction coefficients. For free base porphyrin this yields 1.4 \AA^2 and 0.9 \AA^2 for the Q_x and Q_y bands and 1.9 \AA^2 for the uv band. For the Mg salt the figures are 2.4 \AA^2 and 4.7 \AA^2 for the Q and B bands, respectively. Thus even

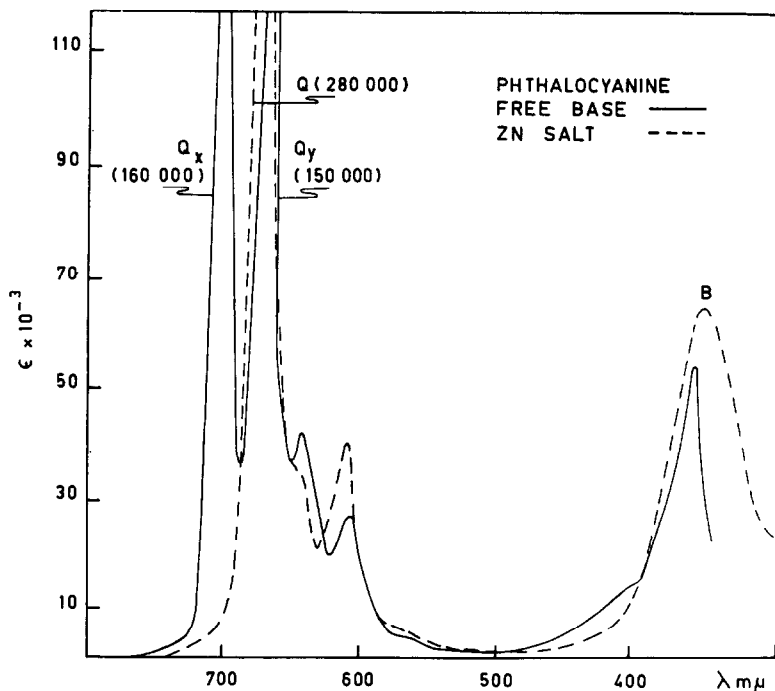


FIG. 14. Absorption spectra of phthalocyanine. Solvents: Free base—chloronaphthalene; Zn-pyridine (Ref. 27).

in free base phthalocyanine the uv bands are not substantially weaker than the visible.

Figure 15 shows tribenztetrazaporphin, free base, and Cu salt. The large asymmetry in the skeleton causes the Q bands to split by 800 cm in the salt, rising to 2000 cm in the free base. This is reasonable in the light of our theory. Finally Fig. 16 shows β -naphthalocyanine free base and Mg- α -naphthalocyanine. Even here the cyclic polyene effect is still evident.

The spectra of Figs. 13 to 16 show quite clearly that the benzporphyrins have spectra basically similar to porphin. That this need not be so is shown by some interesting "conjugated macrocycles" that are reported by Linstead (27). For instance, he reports a compound where two of the pyrrole rings are replaced by pyridine rings. With this molecule the spectrum is shifted far to the blue. Also somewhat relevant is the spectrum of the recently synthesized 18-membered cyclic polyene, whose spectrum in the region 456 m μ to 378 m μ has been interpreted as indicating bond alternation (30). These facts suggest a special stability to the porphyrin ring system, for which present theory provides no clues.

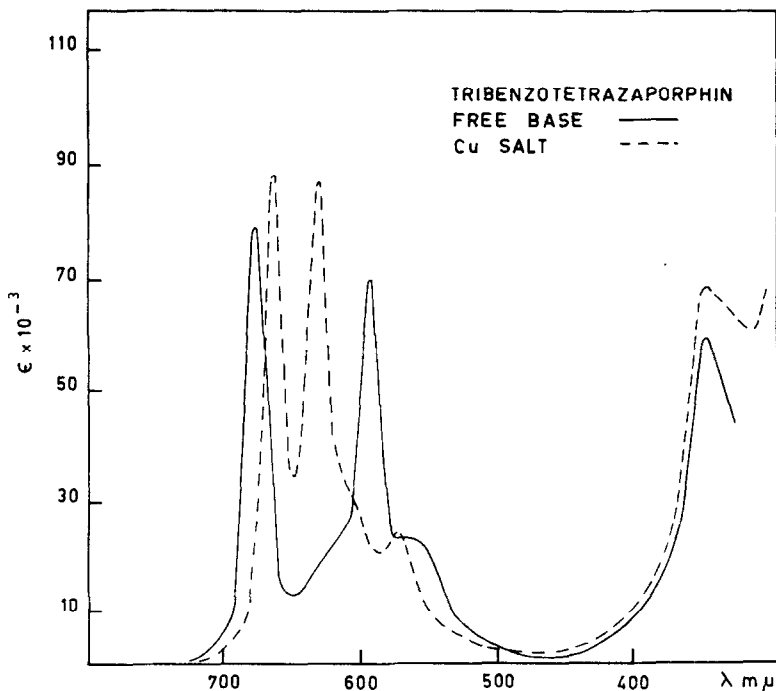


FIG. 15. Absorption spectra of tribenzotetrazaporphin. Solvents: Free base—chlorobenzene; Cu—dichlorobenzene (Ref. 28, 29).

VI. EMISSION SPECTRA

A. FLUORESCENCE AND PHOSPHORESCENCE DATA AND INTERPRETATION

Recently, Allison and Becker (31) published a most beautiful systematic study of the emission spectra of porphins. Their results rearranged, are shown

in Table I. The experimental results fall into three groups. We shall show that the theory for each group is different. The closed shell cases are merely an application of usual spin-orbit coupling. The mechanism for the enhancement by the paramagnetic open shell metals is the same as that recently proposed for oxygen enhancement of singlet-triplet transitions (32-34). In this paper we shall propose a new mechanism for the effect of the diamagnetic open shell metals.

1. Closed Metal Shells

Figure 17 shows the energy levels in the closed shell porphin molecules. We indicate the ground state, $^1A_{1g}$, and the lowest excited states 1E_u and 3E_u . The mixing together of singlets and triplets is due to spin dependent terms in the

TABLE I
LUMINESCENCE AND LIFETIME DATA OF METALLOPORPHYRINS^a

| Compounds | Fluorescence | | Phosphorescence | | Z | Estimated lifetime of triplet state |
|--------------------|---|--------------------|---|--------------------|----|-------------------------------------|
| | Position of 1st band — cm ⁻¹ | Relative Intensity | Position of 1st band — cm ⁻¹ | Relative Intensity | | |
| Closed shell | | | | | | |
| Mesoporphyrin | 16 196 | v.s. | 13 310 | v.w. | 7 | $\geq 5 \times 10^{-4}$ |
| Mg (II) Etiop. | 16 972 | s. | 13 439 | w. | 12 | $\geq 5 \times 10^{-4}$ |
| Zn (II) Mesoporph. | 17 492 | m. | 14 260 | m. | 30 | $\geq 5 \times 10^{-4}$ |
| Cd (II) Mesoporph. | 17 185 | w. | 13 772 | v.s. | 48 | $\geq 5 \times 10^{-4}$ |
| Ba (II) Mesoporph. | 16 780 | v.w. | 13 345 | v.s. | 56 | $\geq 5 \times 10^{-4}$ |
| Open shell | | | | | | |
| Paramagnetic | | | | | | |
| Co (II) Mesoporph. | None | — | 14 908 | v.w. | 27 | $< 5 \times 10^{-4}$ |
| Cu (II) | None | — | 14 665 | v.s. | 29 | $< 5 \times 10^{-4}$ |
| Ag (II) Mesoporph. | Not observed | — | Not observed | — | 47 | — |
| Open shell | | | | | | |
| Diamagnetic | | | | | | |
| Ni (II) Mesoporph. | None | — | 14 680 | v.w. | 28 | $\geq 5 \times 10^{-4}$ |
| Pd (II) Mesoporph. | None | — | 15 200 | v.s. | 46 | $\geq 5 \times 10^{-4}$ |

^a See Ref. 31.

Hamiltonian. These cause the states 1E_u and 3E_u to interact. This interaction gives rise to a radiationless transition from the state $^1E_u \rightarrow ^3E_u$. The latter state is metastable. However, the same coupling allows it to emit.

The strength of spin orbit coupling depends very highly of the atomic number Z of the atoms present. Thus as Z rises phosphorescence should increase at the expense of fluorescence. The data beautifully confirm this idea.

2. Open Shell Paramagnetic Metals

The closed shell metals are divalent. We shall assume that the open shell metals are similarly bound; that is two electrons are involved in the metal porphyrin bonding. In this way we determine the number of electrons in the metal d shell. We shall take the lowest porphyrin states as $^1A_{1g}$, 1E_u , 3E_u , assuming the latter two arise from the transition $a_{2u} \rightarrow e_g$. (A quantitative treatment must, of course, include transitions $a_{1u} \rightarrow e_g$. We ignore these in our argument since their introduction makes the analyses more intricate without substantially altering the conclusion.) Thus a charge transfer donor state will be $^2A_{2u}$.

To discuss the open shell electrons, it is necessary to know the effect of the porphyrin ligand field on the d orbitals. The order among the d levels is debatable. Various orders have been given that have only one thing in common: $d_{z^2-y^2}(b_{1g})$

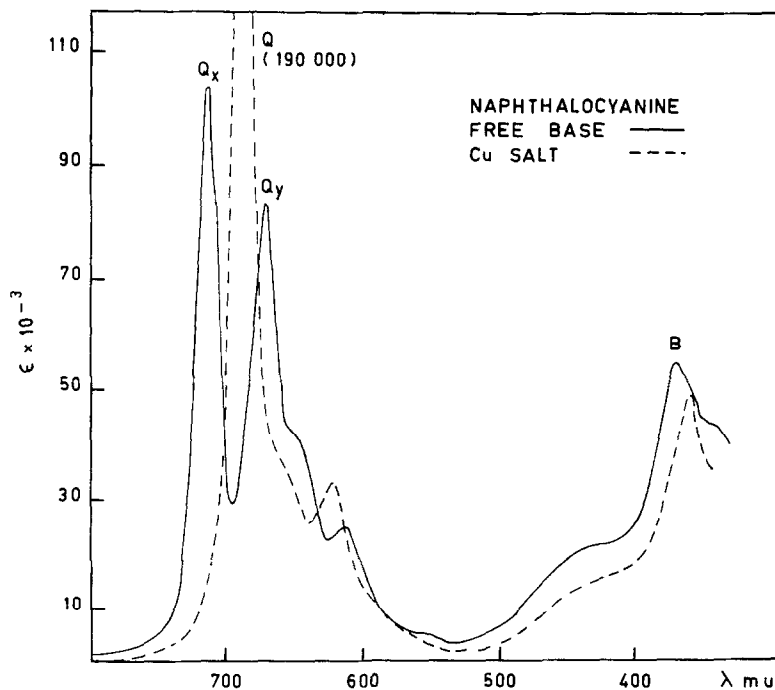


FIG. 16. Absorption spectra of β -naphthalocyanine free base and α naphthalocyanine Cu salt; solvent chloronaphthalene. (Linstead and coworkers; previously unpublished).

is always highest (35). We shall assume this, leaving more detailed discussion to the future. Thus the Cu (d^9) state will be ${}^2B_{2g}$, while a charge transfer acceptor state is ${}^1A_{1g}$.

We shall indicate the Cu porphin states as

$${}^2({}^2B_{1g} \cdot {}^1A_{1g}), \quad {}^2({}^2B_{1g} \cdot {}^3E_u), \quad {}^4({}^2B_{1g} \cdot {}^3E_u),$$

etc., where we indicate the state of the Cu and the porphin separately and the superscript number outside the bracket is the overall multiplicity. Figure 17 shows the states of Cu porphin. (We assume the charge transfer state ${}^2({}^1A_{1g} \cdot {}^2A_{2u})$ is above the others.) There is still a spin orbit coupling as in the closed shell case. The novel effect, however, is the introduction of another doublet ${}^2({}^2B_{1g} \cdot {}^3E_u)$. This latter couples by coulombic exchange terms with ${}^2({}^2B_{1g} \cdot {}^3E_u)$. These terms, much larger than the usual spin orbit coupling term, cause this new state to quench fluorescence. It is an interesting fact that though in other cases coupling with a charge transfer state has been assumed to be the chief source of observed effects (33, 34), in this case it plays no role. For symmetry reasons not only does the charge transfer state not couple with the state ${}^2({}^2B_{1g} \cdot {}^3E_u)$, but the charge transfer state is itself forbidden.

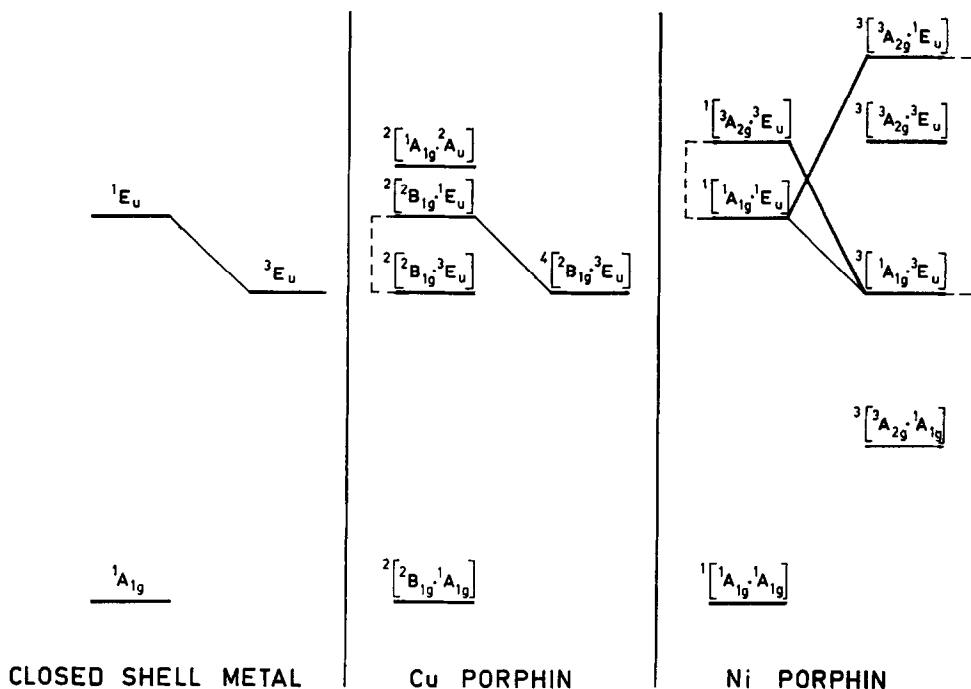


FIG. 17. Energy levels in metal porphins. Dashed lines show coulombic exchange interactions. Thin solid lines usual spin orbit coupling interaction; thick solid lines strong spin orbit coupling.

Other paramagnetic complexes should behave in a similar way. Ag(II), in particular, has an identical set of energy levels. We offer the following suggestion as to why it has no emission. Since divalent Ag is so very rare, it is reasonable to suppose the charge transfer state may be much lower. In particular it might lie between the state $^2({}^2B_{1g} \cdot {}^3E_{1u})$ and the ground state and could provide an intermediate step for radiationless transition to the ground state.

3. Open Shell Diamagnetic Metals

In Ni porphin the lowest configuration is $(d)^8$, spin paired, $^1A_{1g}$ (36). A charge transfer state plays no role, as with Cu, so we omit it. However, Ni should have a low-lying triplet, which we take a ${}^3A_{2g}$, for reasons to be given. Figure 17 shows the energy levels of Ni porphin. Without ${}^3A_{2g}$ the states are just like the closed shell case, with no reason for unusual behavior. We propose a mechanism by which the triplet Ni state can cause observed effects. It has long been known that the spin-orbit coupling in π - π transitions depends on small three center integrals (37, 38). Such integrals directly couple $^1({}^1A_{1g} \cdot {}^1E_u)$ and $^3({}^1A_{1g} \cdot {}^3E_u)$. However, the state $^1({}^1A_{1g} \cdot {}^1E_u)$ can be shown to couple with $^3({}^3A_{2g} \cdot {}^1E_u)$ by a one-center

spin orbit integral on the Ni atom. This latter state couples with the state ${}^3({}^1A_{1g} \cdot {}^3E_u)$ by a coulombic exchange term. Thus the state ${}^3({}^3A_{1g} \cdot {}^1E_u)$ gives rise to an indirect coupling between ${}^1({}^1A_{1g} \cdot {}^1E_u)$ and ${}^3({}^1A_{1g} \cdot {}^3E_{1u})$.³ However, since the spin orbit integral of this indirect link may be perhaps 100 times larger than that of the direct coupling, this mechanism may be of importance in enhancing spin intercombinations.

To get to cases, experimentally the table shows no fluorescence in either Ni or Pd, both of which are (*d*)⁸. We account for this by the enhanced coupling mechanism given above. Ni has a weak phosphorescence Pd a strong one. This we explain by assuming the state ${}^3({}^3A_{2g} \cdot {}^1A_{1g})$ in Ni is so placed as to give a radiationless path to the ground state. Since in Pd the *d* orbitals are more tightly bound, it may be that the ligand field is smaller. Thus ${}^3({}^3A_{2g} \cdot {}^1A_{1g})$ would lie close to the ground state, making the radiationless path less likely.

Finally we note that this mechanism will operate only if the Ni triplet is ${}^3A_{2g}$. On symmetry grounds only ${}^3A_{2g}$ or 3E_g will have a large spin orbit coupling term. However, also on symmetry grounds, only ${}^3A_{2g}$ will give rise to the required coulombic coupling.

B. FUTURE WORK

The study of the porphin emission spectra has really just been opened by the lovely work of Allison and Becker. Quantitative determination of yields and lifetimes of all three series could provide the basis for more detailed theory on all the effects. The theoretical discussion above is also only a first step. It shows, however, the intricacies of the case. Moreover, it shows how emission work can give indirect information on questions about the ligand field that can complement paramagnetic resonance studies (39, 40).

VII. *n*- π SPECTRA

The existence of *n*- π singlet and triplet states in porphyrins is of considerable interest, for such states can markedly alter emission properties (41). Since chlorophyll has carbonyl substituents, such states may play an important role in photosynthesis. Thus the recent discovery of such states by Fernandez and Becker (42) is quite exciting. They were able to produce an unusual emission in chlorophyll in very dry solvents at low temperature. The emission is coincident with the appearance of a shoulder on the chlorophyll absorption spectrum. The data were interpreted as the *n*- π triplet emission and the *n*- π singlet absorption. Many interesting theoretical and experimental questions have been opened by this research. Theoretically the outstanding question is why the *n*- π spectra appear where they do. Experimentally it will be most valuable to determine whether there are restrictions on the carbonyl-group for the spectra to appear.

³ The state ${}^1({}^3A_{2g} \cdot {}^3E_u)$ behaves similarly. See Fig. 17.

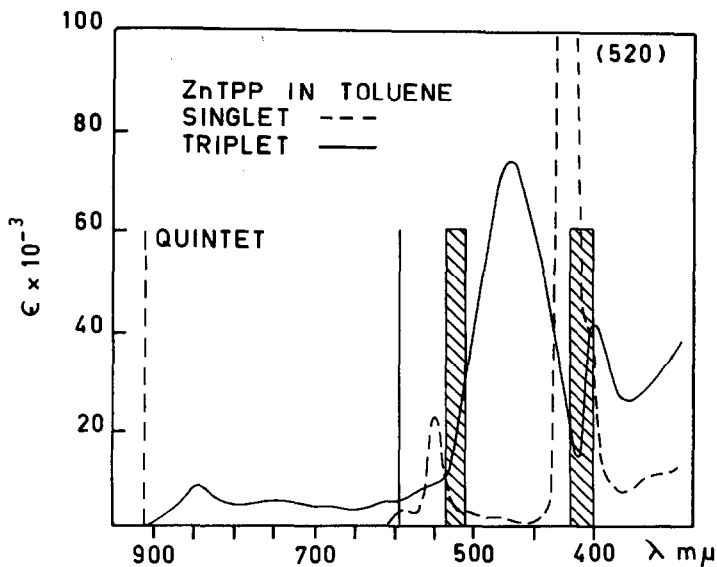


FIG. 18. Triplet-triplet spectrum of Zn tetraphenyl porphyrin. Hatched bars are predicted allowed transitions of intensity proportional to the width of the bar. The line indicates a weakly forbidden singlet (Ref. 44).

VIII. TRIPLET-TRIPLET SPECTRA

Linschitz and coworkers (43, 44) have recently been measuring the triplet-triplet spectra of several porphyrins. "The method used . . . involves the almost complete conversion of the dissolved dye to its metastable state, by means of a brief and intense light flash, and the measurement of the magnitude and time course of resulting spectral changes in the solution using a scanning beam, monochromator, photocell, and oscilloscope (44)." Similar spectra have been reported by other workers (45). A typical spectrum that of Zn tetraphenylporphyrin, is shown in Fig. 18.

The author (46) has developed a theory to explain these spectra. Spectra from the metastable triplet could arise either from: (1) further excitation of the excited electron, (2) further excitation of the hole, or (3) excitation of a second electron. Only for case (3) can it be expected that present theory will give valid predictions. It is assumed that a second electron is excited from orbitals b_1 and b_2 to orbitals c_1 and c_2 . Information from the singlet spectra can then be used to predict the metastable triplet levels. The predictions from case (3) as we shall show below, do explain the observed spectra. The conclusion has therefore been tentatively drawn that most of the observed spectrum arises from double excitation.

The model proceeds from a case of complete degeneracy of orbitals b_1 and b_2 . It then proves convenient to identify the porphyrin orbitals with those of a cir-

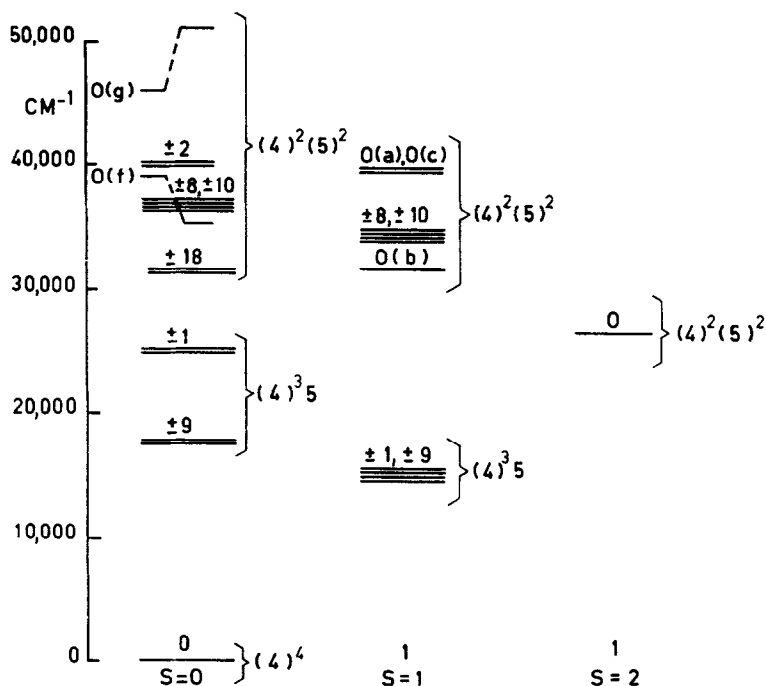


FIG. 19. Predicted energy levels for single and double excitation in porphyrin. S indicates spin. The number on each level are Λ_z values (Ref. 46).

cular box. For the latter, angular momentum is a good quantum number. Because of their nodal behavior, orbitals b_1 and b_2 are taken as having angular momentum along the axis $\lambda_z = \pm 4$, while c_1 and c_2 have $\lambda_z = \pm 5$. In the ground state the $\lambda_z = \pm 4$ orbitals are filled, which is denoted by $(4)^4$. The singly excited states involve one electron in the $\lambda_z = \pm 5$ orbitals, denoted by $(4)^3 5$. The doubly excited states are denoted by $(4)^2(5)^2$. The molecular states will be characterized by a total momentum along the z axis Λ_z . Figure 19 shows the excited states from these three configurations with their total spin S and their Λ_z values.

The detailed discussion shows that the main effect of the nondegeneracy of orbitals b_1 and b_2 will be (for the triplet states) on the states with $\Lambda_z = \pm 1$ and ± 9 . These will split into two pairs of states so that the lowest pair is a 50-50 mixture of the ± 1 and ± 9 Λ_z values. Since selection rules are $\Delta\Lambda_z = \pm 1$ it can be seen from Fig. 19 that transitions to all the $(4)^2(5)^2$ triplet states are allowed. However, the calculation shows that the transition moment to the state labeled $O(b)$ vanishes. This gives the predicted spectrum shown in Fig. 18. The total intensity is just one half the singlet-singlet intensity.

An interesting problem is the free base cyclic polyene perturbation on the

triplet-triplet spectra.⁴ The large effect will be on 9 noded states; the states for which the distinction between nodes through the atoms or through the bonds is important (47). A combination of Figs. 4 and 19 shows that the effect of the cyclic polyene perturbation will be to lift the degeneracy of the $(4)^35$ triplets. The lowest triplet would move to lower energy and would have a larger component of the states with angular momentum ± 9 . The triplet-triplet spectra should therefore shift to the blue, on free base formation, and transitions to the higher momentum doubly excited states would intensify at the expense of transitions to the lower. The first consequence is indeed observed (44). It is not clear whether the latter occurs. The intensity effect should be more pronounced in unsubstituted porphyrin, where the degeneracy between b_1 and b_2 is closer, than in tetraphenylporphyrin, since this lack of degeneracy decreases this intensity effect.

The theory accounts for the triplet-triplet data as well as could be reasonably expected. The weak transitions to the red of those predicted are assigned to higher singly excited states. Accumulation of more data should determine whether this theory is valid.

IX. SUMMARY

This review has discussed the absorption spectra of the various porphyrin compounds. We have shown that present theory gives considerable understanding of the observed spectra. It also gives predictions about polarizations which can be checked. The theory is, however, not on a sound mathematical foundation comparable to that developed for aromatic hydrocarbons. It is hoped that this will be developed in the future. In addition, we have discussed the considerable regularity shown by the emission spectra. It may be anticipated that further studies of emission will be important not only for the porphyrins themselves, but for a basic understanding of spin-intercombinations problems. Finally the discovery of $n-\pi$ states and the recent investigation of triplet-triplet spectra provide new ways to enrich our understanding of excited states in these systems.

ACKNOWLEDGMENTS

I would like to thank Prof. R. B. Woodward for some very stimulating discussions of porphyrin spectra. I would also like to express my gratitude to Dr. G. J. Hoijtink and Mr. C. M. Kooi, who made available the facilities of the Free University of Amsterdam for the completion of this paper, and to the University's very cooperative staff.

RECEIVED: September 9, 1960

REFERENCES

1. R. J. P. WILLIAMS, *Chem. Revs.* **56**, 299 (1956).
2. "Symposium on Haematin Enzymes, Canberra, Australia, 1959" (R. K. Morton, S. E. Falk, and R. Lambert, eds.) Pergamon, London, in preparation.
3. E. RABINOWITCH, *Revs. Modern Phys.* **16**, 226 (1944).

⁴ Investigation of this problem was suggested by J. R. Platt (private communication).

4. G. D. DOROUGH, J. R. MILLER, AND F. M. HUENNEKENS, *J. Am. Chem. Soc.* **73**, 4315 (1951).
5. A. STERN AND CO-WORKERS, *Z. physik. Chem.*, 1934 to 1937.
6. A. STERN AND H. WENDERLEIN, *Z. physik. Chem.* **176A**, 81 (1936).
7. R. P. LINSTAD AND M. WHALLEY, *J. Chem. Soc.* p. 4839 (1952); G. E. FICKEN AND R. P. LINSTAD, *J. Chem. Soc.* p. 4846 (1952).
8. A. STERN AND M. DEZELIC, *Z. physik. Chem.* **180A**, 131 (1937).
9. W. T. SIMPSON, *J. Chem. Phys.* **17**, 1218 (1949).
10. H. C. LONGUET-HIGGINS, C. W. RECTOR, AND J. R. PLATT, *J. Chem. Phys.* **18**, 1174 (1950).
11. J. R. PLATT, "Radiation Biology," A. Hollaender, ed. Vol. III, chapter 2. McGraw Hill, New York, 1956.
12. M. GOUTERMAN, *J. Chem. Phys.* **30**, 1139 (1959).
13. M. J. S. DEWAR AND H. C. LONGUET-HIGGINS, *Proc. Phys. Soc.* **67A**, 795 (1954).
14. W. MOFFITT, *J. Chem. Phys.* **22**, 320 (1954).
15. R. PARISER AND R. PARR, *J. Chem. Phys.* **21**, 767 (1953); R. PARISER, *J. Chem. Phys.* **24**, 250 (1956).
16. N. S. HAM AND K. RUEDENBERG, *J. Chem. Phys.* **25**, 1, 13 (1956); **29**, 1199, 1215 (1958).
17. S. L. MATLOW, *J. Chem. Phys.* **23**, 673 (1955).
18. J. R. BARNARD AND L. M. JACKMAN, *J. Chem. Soc.* 1172 (1956).
19. G. R. SEELY, *J. Chem. Phys.* **27**, 125 (1957).
20. J. W. WEIGL, *J. Mol. Spectroscopy* **1**, 133 (1957).
21. C. RIMINGTON, S. F. MASON, AND O. KENNARD, *Spectrochim. Acta* **12**, 65 (1958).
22. R. B. WOODWARD (private communication).
23. L. GOODMAN AND R. W. HARRELL, *J. Chem. Phys.* **30**, 1131 (1959).
24. H. KOBAYASHI, *J. Chem. Phys.* **30**, 1362, 1373 (1959).
25. G. D. DOROUGH AND F. M. HUENNEKENS, *J. Am. Chem. Soc.* **74**, 3974 (1952).
26. R. STUPP AND H. KUHN, *Helv. Chim. Acta* **35**, 2469 (1952).
27. R. P. LINSTAD, *J. Chem. Soc.* p. 2873 (1953).
28. J. A. ELVIDGE AND R. P. LINSTAD, *J. Chem. Soc.* p. 3536 (1955).
29. J. A. ELVIDGE, J. H. GOLDEN, AND R. P. LINSTAD, *J. Chem. Soc.* p. 2466 (1957).
30. M. GOUTERMAN AND G. WAGNIÈRE, *Tetrahedron Letters* **8**, 22 (1960).
31. J. B. ALLISON AND R. S. BECKER, *J. Chem. Phys.* **32**, 1410 (1960).
32. G. J. HOIJTINK, *Mol. Phys.* **3**, 67 (1960).
33. R. S. MULLIKEN AND TSUBOMURA, *J. Am. Chem. Soc.* in press (1960).
34. J. MURRELL, *Mol. Phys.* **3**, 319 (1960).
35. L. E. ORGEL AND J. S. GRIFFITH, in "Symposium on Haematin Enzymes, Canberra, Australia, 1959." (See reference 2.)
36. G. MAKI, *J. Chem. Phys.* **28**, 651 (1958).
37. D. S. McCCLURE, *J. Chem. Phys.* **20**, 682 (1952).
38. J. W. SIDMAN, *J. Chem. Phys.* **29**, 644 (1958).
39. J. E. BENNETT, D. J. E. INGRAM, P. GEORGE, AND J. S. GRIFFITH, *Nature* **176**, 394 (1955).
40. J. E. BENNETT AND D. J. E. INGRAM, *Nature* **177**, 275 (1956).
41. J. W. SIDMAN, *Chem. Revs.* **58**, 689 (1958).
42. J. FERNANDEZ AND R. BECKER, *J. Chem. Phys.* **31**, 467 (1959).
43. H. LINSCHITZ AND K. SARKANEN, *J. Am. Chem. Soc.* **80**, 4826 (1958).
44. H. LINSCHITZ AND L. PEKKARINEN, *J. Am. Chem. Soc.* **82**, 2411 (1960).
45. R. LIVINGSTON, *J. Am. Chem. Soc.* **77**, 2179 (1955).
46. M. GOUTERMAN, *J. Chem. Phys.* **33**, 1523 (1960).
47. J. PLATT, *J. Chem. Phys.* **17**, 484 (1949).