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THE PI ELECTRON ABSORPTION SPECTRA OF CHLOROPHYLLS IN SOLUTION

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Abstract

This paper reviews the spectra of and proposes new assignments for the electronic absorption spectra of protochlorophyll, chlorophyll a, bacteriochlorophyll a and their respective pheophytins. The assignments are based on a detailed comparison of absorption, fluorescence polarization, circular dichroism (CD), and magnetic circular dichroism (MCD) spectra in the visible and ultra-violet with the well understood spectra of the unsubstituted parent rings. Pariser-Parr self-consistent molecular orbital calculations are used for guidance. Chlorophylls b and d are briefly considered.

Our assignments agree with earlier work on the Q_x and Q_y transitions in the visible region. Extensive configuration interaction calculations confirm that these can be treated within the limited CI framework of the Gouterman four-orbital model, much as in porphyrins. The Soret band of chlorin and ADJ-tetrahydroporphin, but not that of OPP-tetrahydroporphin, can also be represented by the four-orbital model.

In the ultraviolet beyond the Soret region, we have identified in protochlorophyll an eta band analogous to those previously found in metal 2,4-diacetyl deuteroporphyrins. This band is identified with the theoretically predicted $(1a_{1u}2b_{1u})$ and $(3a_{2u}2b_{1u})$ transitions. The Soret band of protochlorophyll

a may contain more than two transitions, in accordance with a suggestion of Song.

Previous workers assigned the chlorophyll *a* and pheophytin *a* Soret bands and their first satellites to B_x and B_y states, respectively. Newly available MCD spectra indicate instead that the B transitions are accidentally degenerate and together produce the major Soret peak. The B_x contributes more intensity than does the B_y. A new pi-pi* transition, which we name eta for convenience although it is of mixed parentage, produces the satellite on the major Soret peak previously assigned to the B_y transition. This new band becomes allowed by reason of the combined perturbations of carbonyl substitution and ring distortion by the isocyclic ring. It disappears if the isocyclic ring is cleaved or if its carbonyl group is reduced. The ultra-violet spectrum of chlorophyll *a* is complicated in origin because of the low symmetry of the parent chlorin ring. These interpretations are based more on examination of the data than on calculations.

The Soret band of bacteriochlorophyll displays dramatic solvent effects in which five bands interchange intensity. Our calculations and those of Song indicate that at least three allowed and two forbidden transitions lie in this region. The ultra-violet absorption of bacteriochlorophyll beyond the Soret band may be due to ring distortion and vibronic borrowing. The lowest triplet of bacteriochlorophyll is predicted to be only 5500-7100 cm^{-1} above the ground state.

Calculations of the spectroscopic effects of ring reduction and substitution agree fairly well with experiment. In particular, the "480 nm" band recently identified in free base porphyrins is predicted to occur in free base chlorins and pheophytins, and in fact can be found in their spectra. Predicted shifts in ground state charge density upon carbonyl substitution agree qualitatively with data on CO stretch frequencies of carbon monoxy-hemes and with association constants of nickel porphyrin pyridinates. Transition monopoles are calculated for the visible transitions of chlorophyll *a* and bacteriochlorophyll *a*, for use in calculations of monomer and dimer absorption and CD spectra and of intermolecular interaction matrix elements.

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A longstanding aim of the molecular orbital theory of porphyrins has been approximate wave functions for the ground and excited states of the chlorophylls good enough to support a definitive assignment of the absorption spectra. Such wave functions would supply the quantum chemist's answer to the old question of why grass is green. They would be valuable, among other things, in calculating the properties of chlorophylls in aggregated states related to their structure _in vivo_.

The self-consistent molecular orbital theory of Pariser, Parr and Pople (SCMO-PPP) (1,2) has made it relatively easy to perform approximate calculations on π electron systems even as large as that of chlorophyll. The results of these calculations depend on moderately severe assumptions and mildly arbitrary input parameters, and it is best to approach them with some skepticism. One test of the validity of the calculations on such a highly substituted chemical species is to start with a simpler related molecule whose properties are thought to be well understood, and to build up to a model of the desired molecule by adding chemical perturbations one by one. The chlorophylls are particularly suited to such an approach, as their parent rings the porphyrins have been subjected to extensive theoretical analysis, the results of which have been thoroughly compared with experiment. (3,4,5,6,7) Moreover, experimental data on a large number of substituted porphyrins and reduced porphyrins are available to enable one to trace the experimental effects of these chemical modifications.

The present study began as a preliminary attempt to extend to carbonyl substituted porphyrins, among which are the chlorophylls, the extensive SCMO-PPP calculations we previously performed on porphyrins and larger macrocycles.(6,7) The effects of substitution are much subtler than those of ring reduction, and we found it necessary to gather many more spectra than had been used in our previous comparisions between theory and experiment. Careful comparison of the absorption spectra of closely related molecules, plus qualitative interpretations of newly available magnetic circular dichroism (MCD) spectra, led us to revise a number of long accepted spectroscopic assignments and to propose several new ones. We compared our calculated results with our newly expanded phenomenological interpretations of the data, and found that they agreed moderately well.

Introductory Survey

By "the chlorophylls" we shall in this review mean the molecules protochlorophyll a, chlorophyll a, and bacteriochlorophyll a. These are derived from the parent rings porphin, chlorin (dihydroporphin), and bacteriochlorin (OPP-tetrahydroporphin), respectively. Chlorin is derived from porphin by the reduction of one double bond, and bacteriochlorin by the reduction of double bonds from each of two opposite pyrrole rings. One of the isomers of bacteriochlorin has two double bonds reduced on adjacent pyrrole rings, and is known as ADJ-tetrahydroporphin or hypochlorin.(8) These molecules are known collectively as porphyrins, a generic term which can also include larger macrocycles like the tetrabenzoporphyrins and phthalocyanines. The formulas for a number of photosynthetic pigments are shown in Fig. 1.

The porphyrin ring carries an excess of two electrons, which may be neutralized by a divalent metal ion (in chlorophylls, magnesium) to form the metalloporphyrins. Alternatively, two of the central nitrogens may bond to hydrogen atoms to form the free base. Structures of some free bases related to chlorophyll *a* are shown in Table I.(8,9) With a few exceptions, the general features of the spectrum of a given ring are constant from metal to metal. Energies and relative intensities show some variation, but only within a well-defined pattern.(3) Present methods of excited state calculations are only beginning to distinguish well between one metal and another. (10,11)

Spectra of photosynthetic porphyrins in solution at varying levels of oxidation are shown in Figs. 2 and 3. Fig. 2 shows the spectra of protochlorophyll *a* and chlorophyll *a*; Fig. 3, of bacteriochlorophyll *a* and 2-desvinyl-2-acetyl chlorophyll

a. Each compound of each pair is identical to the other except for the reduction of a double bond. The spectrum of the ADJ-THP analog of chlorophyll, called hypochlorophyll, is given in reference 15. (See Fig. 8 below.) All these molecules show an intense absorption in the blue or near ultra-violet region, the so-called Soret band, and bands of lower oscillator strength (though occasionally greater extinction coefficient) in the visible or near infra-red.

These bands are due entirely to pi-pi* excitations within the conjugated macrocycle. The solution spectra of the chlorophylls have been reviewed many times, (16) most recently by Goedheer (17) and by Gurinovitch, Sevchencko and Solov'ev.(18) The latter review includes a discussion of high resolution spectra of porphyrins and chlorins taken at low temperature, an area which we shall not consider here.

The hypothesis that low-lying n-π* excited states may play a role in chlorophyll a spectroscopy has re-appeared from time to time, most recently in ref. 19. Early evidence presented in favor of n-π* absorption in the visible region is reviewed and rejected by Gurinovitch.(18) More recently, the observation of quasi-line spectra in ethyl chlorophyllide a (20) excludes such transitions at wavelengths longer than 667 nm. Further work along these lines would be very useful.

The basis for the interpretation of these spectra is the four orbital model of Gouterman, (3,4) who built on earlier work by Moffitt(21)and Platt.(22) An essentially equivalent interpretation, based on the free electron model, has been made by Kuhn(23). The Gouterman model is a limited configuration interaction model, in which the visible and near ultra-violet transitions are assumed to derive from the interaction of the lowest four excited configurations in the singlet pi-pi* manifold. The early history of the theory of porphyrin spectra has been thoroughly reviewed by Gurinovitch. (18)

In the Gouterman model as originally introduced,(3,4) excited states corresponding to the visible and near ultra-violet absorption bands are interpreted phenomenologically as arising from electronic excitation from the highest two filled orbitals to the lowest two empty orbitals. The lowest empty e_{gx} and e_{gy} orbitals are degenerate by symmetry in metal porphyrins, while the highest filled a_{1u} and a_{2u} orbitals are almost degenerate accidentally, i.e., for reasons other than symmetry. (Fig. 4.) The $(a_{1u}e_g)$ and $(a_{2u}e_g)$ configurations interact pairwise to give plus and minus states in which the equal transition dipoles cancel and reinforce each other, respectively. (Configurations are singlets unless otherwise indicated.) This gives rise to a weak, "parity forbidden" Q transition and a very intense "parity allowed" B transition, (Fig. 5), corresponding to the visible and Soret bands, respectively. The major features of the Gouterman model have been confirmed by extensive and careful experiments by the Russian school of spectroscopists. (18)

In later refinements, Gouterman and the Perrins found that the intensity of the overtones of the visible band is "borrowed" from the Soret band by vibrations of the inner 16-membered ring of the porphyrin. (24) Fluorescence polarization measurements (12,25,26,18) indicate that the spectrum in this region is of mixed polarization. This is attributed to the fact that vibrations are available of symmetry appropriate to the borrowing of either x- or y-polarized intensity. The old classification of substituted free base porphyrins into "spectral types" (etio, rhodo, chloro, etc.) (27) rests on the fact that the intrinsic (0-0) intensities of the Q_x and Q_y bands* of the free base are very sensitive to substituents, while the "borrowed" intensity of the vibrational overtones is relatively insensitive to these perturbations. The theoretical basis for these spectral types was outlined by Gouterman (3) and is discussed in detail by Gurinovitch *et al.* (18)

Hückel calculations of porphin MO energies did not give the accidental degeneracy, required by experiment, between the $1a_{1u}$ and $3a_{2u}$ orbitals. (28) Gouterman (4,5) adjusted the

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*The Q_x and Q_y are the first and third of the typical four-banded spectrum of free base porphyrins, respectively. The H-H axis is the x axis.

energies of these two orbitals to give the required degeneracy, and found that the Huckel orbitals were then an excellent starting point for extending his phenomenological model to reduced porphyrins and other macrocycles. The resulting MO energies are shown in Figure 4a.

Later SCMO-PPP calculations by Weiss et al (6) gave $1a_{1u}$ and $3a_{2u}$ orbitals closer to degeneracy (Figure 4b). Two-electron integrals, which represent the attractive interaction between the excited electron and the hole left behind in the valence orbital, were greater for $(1a_{1u}4e_g)$ excitations than for $(3a_{2u}4e_g)$. This effect brought the $(1a_{1u}4e_g)$ and $(3a_{2u}4e_g)$ configurations into almost exact degeneracy for three different choices of input parameters, substantiating Gouterman's original conjecture. It would be very useful to confirm these orbital energies by high resolution photoelectron spectroscopy. (29)

This predicted degeneracy put the Gouterman model on a sound theoretical basis, and at the same time restored confidence in Huckel orbitals for non-spectroscopic applications where two-electron terms are not important. The calculations gave good qualitative agreement with the porphyrin triplet-triplet absorption spectrum, as well as the ordinary visible and near ultra-violet absorption spectra of a wide variety of porphyrin derivatives, including azaporphyrins, phlorins, reduced porphyrins, tetrabenzoporphyrins, and phthalocyanines. Felton has used much the same parameters in calculations on the porphyrin radical mono- and di- -anion (30) and -cation (31), as well as on isoporphyrin (32) and isophlorin. (33)

When one or more of the porphin double bonds is reduced to form a chlorin or a tetrahydroporphyrin, the energies of the e_{gy} and, to a lesser extent, the a_{1u} orbitals are raised (Fig. 4), because these orbitals in porphyrin have substantial electron density on the carbons whose double bond is to be reduced. The energies of the e_{gx} and a_{2u} orbitals, which do not have electron density on these carbons, are slightly lowered on reduction. (34,4,6) These effects are clearly displayed in the arbitrarily adjusted Hückel orbital energies of Figure 4a. (4) In particular, the energy splitting between the e_g bands in chlorin is almost exactly the same as that between the a_{2u} and a_{1u}.* The pattern of energy shifts of SCMO-PPP orbitals of Figure 4b is similar, although these splittings are unequal.

The main features of four orbital SCMO calculations of metal porphin are not affected by such theoretical refinements as changes in parameters, (35) changes in geometry, (6,10) use of the variable electronegativity method, (36,37) inclusion of non-nearest neighbor resonance integrals, (37) and configuration interaction including all singly excited configurations. (7) McHugh *et al* (7) have extended these calculations to the far ultra-violet absorption spectra of these

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*We have abandoned the b_1 b_2 c_1 c_2 orbital labeling used by Gouterman (4) for the four orbitals, and refer to all orbitals by their group theoretical labels in the square symmetry of porphin whenever possible. Orbitals were traced from porphin to derivatives of lower symmetry by noting similarities in energy and nodal distribution.

molecules and to their MCD spectra in the visible and near ultra-violet. They improved the agreement of their predicted oscillator strengths with experiment by using transition gradients instead of transition dipoles.

The spectra of free base porphins are traditionally assigned by analogy with the metal porphins. The four main transitions in the visible are assigned to Q_x and Q_y daughters of the metal porphin Q band, and the B_x and B_y transitions underlying the Soret band are assumed still to be degenerate, by analogy to the 18-membered cyclic polyene.(3) Four-orbital model calculations do not agree with this assignment without fudging.(6) Sundbom(38) achieved improved agreement with experimental bond distances and visible absorption spectra for this molecule by using a refinement, due to Fischer-Hjälmars and her school, of the SCMO-PPP method. Sundbom suggested a reassignment of the Soret region of free base porphin which makes it more complicated in origin than the doubly degenerate Soret band of square metal porphins. In her interpretation, three electronic transitions underlie the Soret band of porphin free base: B_x, B_y and N_x. The B_y has about the same oscillator strength as in metal porphins, but the B_x and N_x each have about half that amount. Experimental absorption and MCD spectra are consistent with this conclusion, if the N_x is much broader than the two B transitions.

McHugh et al (7) agree that there are three transitions in the Soret region, but present evidence for a different assignment. Extending a proposal by F. Longo, they suggest that the extra transition may appear as a band at 480 nm long known by porphyrin chemists to wax and wane in intensity according to the substituents. This variation is thought to be caused by changes in intensity borrowing from the Soret band by a previously unsuspected x-polarized transition.

The spectra of reduced porphyrins have, until recently, received little theoretical attention. Weiss et al (6) published four-orbital model SCMO calculations of metal chlorin, phlorin, OPP-THP, and ADJ-THP, and achieved qualitative agreement with experimental spectra. Their paper reviews earlier Hückel calculations on these unsubstituted rings. The Weiss treatment was extended by McHugh et al (7) and by Otten (39) to include more configuration interaction. Katz et al (40) reported ground state Huckel and SCMO calculations of chlorophyll a, and compared predicted charge densities and electrophilic and nucleophilic localization energies with rates of hydrogen exchange with solvent. Agreement was not good. Since the completion of the work described in the present report, Song (41) presented SCMO-CI calculations of the excited state manifolds of protochlorophyll, chlorophyll a, chlorophyll b, chlorophyll d, and bacteriochlorophyll a, and achieved improved agreement with experimental energies. Otten (39) has done similar calculations on the bacteriochlorin radical cation and anion, while Knop and Fuhrhop (42) have discussed the chemical properties of reduced porphyrins in terms of the molecular orbitals of the unsubstituted rings.

At the same time as the theory of porphyrin spectra has been advancing, data has become available on the absorption, fluorescence polarization, CD and MCD of families of chlorophyll derivatives.(12,9,13) While a number of potentially informative compounds have yet to be studied quantitatively, sufficient data is available to allow much improved comparison between theory and experiment.

In the visible transitions in porphyrins, x- and y-polarized transitions have opposite signs in MCD spectra and usually in CD spectra as well. The reasons for this are different in MCD and CD, and cannot be explained in a simple "physical" picture. (7,13) The MCD of an isolated doubly degenerate transition typically resembles the derivative of the absorption band. The cross-over, or zero point of a double MCD should coincide with the absorption maximum in the case of an isolated doubly degenerate band. For two nearly degenerate transitions, the cross-over should lie between the two absorption maxima.

No transition is truly isolated, and we may expect deviations from these ideal shapes due to interaction with higher and lower states. Furthermore, direct measurement of the absorption of left- and right-handed circularly polarized light (LHCP and RHCP, respectively) by several metal porphyrins in a magnetic field show that the peak of the LHCP absorption is slightly less intense than that of the RHCP absorption. This produces a slight deviation from the symmetrical derivative curve of the MCD spectrum measured as a direct difference between LHCP and RHCP absorption. (24,43,44,45) In more complex bands, this effect could complicate interpretation based on ideal single and double MCD patterns. Still, as we shall see, MCD is very valuable in resolving overlapping or degenerate transitions of mutually perpendicular polarization.

THEORETICAL METHODS

The well known approximations in the SCMO-PPP-CI theory used in this work are as follows: (1,2) 1) Molecular orbitals are expressed as linear combinations of atomic orbitals; 2) Sigma cores are assumed to be rigid and non-polarizable; 3) the zero differential overlap approximation is used to reduce drastically the number of integrals to be computed; 4) semi-empirical parameters are used to correct known deficiencies in computed values of certain integrals. Such an approximate calculation must stand or fall on its ability to inspire interesting experiments and (to a slightly lesser extent) to predict their results.

The parameters and geometry of the porphyrin ring used in most of these calculations were taken from our earlier work (6) to facilitate comparison. CO bond distances were taken as 1.215 Å from X-ray data of Hoard (46) on nickel diacetyl deuteroporphyrin. "Traditional" values were used for carbon and nitrogen parameters.(6) These differ somewhat from the "standard" parameters used for reduced porphyrins in reference 6. The valence state ionization potential and electron affinity of oxygen were taken from Miller.(47) Two values for the resonance integral β_{CO} were used. One, $\beta_{CO} = -3.19$ eV, resulted from setting β_{CO} equal to the value of β_{CC} for the same internuclear distance. The other value, $\beta_{CO} = -2.36$ eV, was taken from Leibovici and Deschamps.(48) These values span the highest and lowest values in the literature, up to 1967. Qualitative conclusions were independent of the choice of β_{CO}. Since we intended these calculations as a preliminary survey to guide both experiments and more detailed theoretical investigation, we made no serious attempt to refine these parameters further.

Alkyl substituents (including the phenyl groups of tetraphenyl porphyrins) and distortions of the ring due to the isocyclic ring of chlorophyll derivatives were ignored in most of the present calculations. Each nitrogen was given 1.5 pi electrons initially to insure electroneutrality and the right number of pi electrons; the central metal was not considered explicitly.

Toward the end of the research, we attempted to include effects of ring distortion in calculations meant to simulate chlorophyll a. For this we used the geometry of methyl pheophorbide a recently determined by Fischer et al.(49) SCMO-PPP-CI calculations of free base chlorin were performed using the "$\Delta\alpha = 5.5$" parameters of McHugh et al. (7) In some calculations, the oxygen was brought into closer conjugation with the ring by use of the oxygen parameters of Tichý. (50)

Calculations were usually performed in two stages: four-orbital model and "extended configuration interaction." In the latter, the basis set was arbitrarily cut off at about 150 nm to stay within the capacity of the computer. Whenever possible, the cutoff was made at a natural break in the density of electronic states. Typical CI calculations included 60-75 configurations, depending on the molecule. The programs used in these calculations were written by W. Donath, expanded by C. Weiss, (35) and further improved by P. Miller and J. Weeks.

Experimental oscillator strengths were estimated from unresolved published data by the formula

$$f = 4.61 \times 10^{-9} \epsilon \delta$$

where ϵ is the molar extinction coefficient and δ the band width at half height, measured in wave numbers. This "triangle" formula is exact only for bands of perfect Gaussian shape. Intensity measurements on closely spaced bands depend on more or less arbitrary decisions about where one band ends and another begins. The usual curve-fitting devices are of limited use here for want of a reliable theory of line shapes to tell us what kind of curve to fit to the data. For this reason, we have not tried to improve on the "triangle" formula.

RESULTS

A. Unsubstituted Reduced Metal Porphyrins: Theory and Experiment

Fig. 5 shows the energy level diagrams for the lower excited states of the reduced metal porphyrins given by the SCMO-PPP-CI calculations. The result is displayed at each of three steps: a) pure configuration energies, corresponding to the length of the arrows in Fig. 4b, less two-electron terms; b) minimum CI; c) extensive CI involving 60-75 configurations. The first two columns agree with the four-orbital results of reference 6, since fairly similar parameters were used in the two calculations.

The shifts in orbital energy on reduction (Fig. 4) destroy the near-degeneracy of the lowest excited configurations (Fig. 5). In the Hückel model (Fig. 4A), the x-configurations in chlorin are still degenerate, and their transition dipoles cancel and reinforce each other, as in porphin, to produce the weak Q_x and the strong B_x, respectively.(5) The Q_y band is therefore predicted to be more intense in chlorin than it is in porphin.

This pattern is retained in the SCMO models. Contrary to the hopes of the early theorists (5), however, the subtle effects of the new terms introduced in this model vary from porphyrin to porphyrin. This probably dashes hopes for a simple parameterized theory to explain reduced porphyrin spectra without the use of MO calculations, along the lines of Ref. 3.

In OPP-THP, where the relative shifts in a_{1u} and a_{2u} orbital energies are more than doubled, the Q_y band is further red shifted and intensified, and the B_y is at higher energy than the B_x. The x-polarized configurations, on the other hand, are more nearly degenerate, and again interact to give a weak Q_x band. (The high intensity normally associated with B_x is distributed among several interacting x-polarized transitions.)

The fact that the more reduced compound absorbs at longer wavelengths may surprise chemists accustomed to the rule of thumb that the smaller the conjugated system the higher the absorption energy. This rule derives from the energy levels of a one-dimensional potential well, and cannot be used to compare two-dimensional systems like porphin and OPP-THP, in which configuration interation plays a central role. These molecules show CI patterns typical of "round-field" and "long-field" molecules, respectively.(28) On the other hand, the "electron-in-a-box" model correctly predicts that the longer wavelength transition in reduced porphins is allowed along the axis with the fewer reduced pyrrole rings.

All of the effects of ring reduction may well be greater in the real molecule than in the SCMO-PPP representation of it, because the CI integrals are already so overestimated in porphyrin that the small but important effects of ring reduction may not make much difference to the model. Even so, the configurational purity of the lowest excited state, calculated in the four-orbital model, rises from 52% in porphin to 68% in chlorin and 84% in OPP-THP.

Adding more configurations to those of the four orbital model has little effect on the energy or intensity of the Q bands of any of these porphyrins. All the Q states are derived at least 97% from four-orbital model configurations. In chlorin and ADJ-THP, the B bands are derived 87% and 95% from four-orbital model states, respectively, compared to 84% in porphin. Configuration interaction integrals between pairs of four-orbital configurations vary almost 100% from porphyrin to OPP-THP, in contrast to the hopeful assumption made in earlier work. (5) The transition dipole of a particular transition, however, varies only about ±20%.

The most accurate way to compare these results to experiment is to consider quantitative spectra of a series of porphyrins with the same substituents, taken in the same solvent, but differing in the level of reduction of the porphyrin ring. Figure 6a-c shows the most suitable matched data in the literature for porphyrins with symmetrically disposed saturated or <u>meso</u>-aryl substituents; Figure 8 below shows similar data for chlorophyll <u>a</u> and bacteriochlorophyll analogs. These sets of spectra are fuller than those used in previous tests of theoretical models, but none of the sequences is complete. Probably the most important lack is the ultra-violet and quantitative visible spectrum of a symmetrically substituted metal OPP-THP.

It is still more difficult to compare theory and experiment because we do not really know to which metal porphyrins our calculations correspond, and the ratio of Soret to visible intensities (especially in porphin) depends strongly on the identity of the central metal. From this point of view, the zinc porphyrin sequence of Figure 6c seems to correspond the most closely of the three to the calculations, since its <u>Q</u> transition is almost parity forbidden. In this section, we will compare the results of calculations on the unsubstituted rings with the data in Figure 6a-c.

The assignments of the visible spectrum are the same as in previous work, and the calculations agree about as well as before.(5,6) Experimentally, the Q_y band in the chlorin is much more intense than the doubly degenerate Q band in porphin. This is correctly reproduced in the calculations. The Q_y also shifted to lower energy. The Q_x band of chlorin is stronger than the porphin Q in three of the four series, but is not strong enough to stand out from the vibrational overtones of the Q_y. Its energy is about the same as that of the porphin Q. The calculations in Figure 5 do not reproduce these trends very well. The chlorin B bands are predicted to come at the same energy as those of porphin, and are in fact so found. The CI pattern of chlorin and hence its spectrum is somewhat similar to that of tetrabenzoporphin. (6,7,59)

For OPP-THP, we must rely mostly on the spectrum of bacteriochlorophyll in Fig. 3. Both bacteriochlorophyll and Mg tetraphenyl OPP-THP (Fig. 5) have the Q_y so red-shifted from the corresponding chlorins, that the Q_x is easily identified by fluorescence polarization. (17) This shift is qualitatively reproduced in the calculations, although it is underestimated.

The calculation correctly predicts that B_x and B_y are accidentally almost degenerate in unsubstituted metal chlorins. The B_y is 260 cm^{-1} above the B_x in the four-orbital model, but 170 cm^{-1} below it in extended CI. (X-allowed states are not constrained by symmetry and will be lowered by configuration interaction more than y-allowed states.) The calculated energy order of $\underline{B}_x$ and $\underline{B}_y$ is not affected by extension of the CI basis set in substituted chlorins. The B-Q energy splitting is overestimated, as in our previous calculations and those of all other workers.* $\underline{B}_x$ and $\underline{B}_y$ are predicted to split in OPP-THP and its unsubstituted derivatives, a prediction in agreement with the spectrum of bacteriochlorophyll in Fig. 3.

The orbital pattern for ADJ-THP is calculated by Hückel and SCMO methods to be similar to that of chlorin, a prediction borne out by the similarity of the available ADJ-THP spectra to those of the corresponding chlorins.(53,58,60) The Q bands are found at energies slightly higher than the corresponding bands in chlorin, a result also given by the calculation. The Soret band of ADJ-THP is predicted to be practically degenerate in the four orbital model, both in the "standard" and in the "traditional" treatment. (6) Extended CI increases this splitting from 54 to 260 cm^{-1}, and predicts that the y band will be higher in energy (see Ref. 3 for axes). The experimental value of the B splitting is 420 cm^{-1}. (58,53) It would be interesting to confirm these assignments by fluorescence polarization and MCD.

We see, then, that the four-orbital model correctly accounts for intensity differences among reduced metalloporphyrin spectra

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*A previous paper (61) concluded that SCMO-PPP calculations overestimated the BQ splitting in 18-annulene, and that this presumed failure represented a general defect in the method. Supsequent measurements found a new state just where theory predicted it, so that the supposed overestimate was probably due to a misassignment of experimental spectra. (62) We must therefore look elsewhere for an explanation of the B-Q overestimate in porphyrins.

in the visible and Soret regions, but does not do very well at predicting quantitative energy shifts. This result is largely unaffected by increased configuration interaction. This suggests that the four-orbital model is essentially correct, but that our quantitative representation by the SCMO-PPP-CI model is inadequate. The consistent overestimation of the *B*-*Q* splitting suggests that the fault is in the CI treatment. In fact, the pure configuration energies of Fig. 5 reproduce the experimental energy shifts of the visible bands better than do the post-CI state energies.

The Soret region of OPP-THP cannot be described by the four-orbital model. According to our calculation (Fig. 5), it includes three allowed and two forbidden bands, instead of the two allowed bands characteristic of the other unsubstituted metal porphyrins. The theoretical origin of the new allowed band is as follows. We have already seen that the $4e_{gy}$ orbitals of porphyrin are raised sharply in energy on reduction to OPP-tetrahydroporphyrin. This raises the energies of the $(1a_{1u}4e_{gy})$ and $(3a_{2u}4e_{gy})$ configurations so high that transitions to the $4e_{gy}$ from a new orbital, denoted *a* in Fig. 4b, are only slightly higher in energy. The *a* orbital is a descendant of the $2a_{2u}$ and $2b_{2u}$ orbitals in porphin. Since the transitions $(2a_{2u}4e_{g})$ and $(2b_{2u}4e_{g})$ interact to form the *L* and *N* bands of porphin, (6) the (ae_{gy}) bands of chlorin and OPP-THP have been named

N. The N_y bands of the reduced porphyrins are split to higher energies by configuration interaction. Only the N_x is important to the present discussion.

In chlorin, N_y is predicted to be the first moderately intense band above the Soret. In OPP-THP, by contrast, configuration interaction splits the B bands to higher energy than that of the (ae_{gy}) configuration, so that the N_x band is predicted to appear as a shoulder on the long wavelength side of the Soret band. Calculations to be described in a later section extend this prediction to bacteriochlorophyll.

We do not have available the Soret band of an unsubstituted or symmetrically substituted OPP-THP to compare with these results. Absorption spectra of bacteriochlorophyll *a* in each of four solvents are shown in Fig. 7. We shall defer detailed discussion of these spectra until a later section, except to draw attention to the complex, solvent dependent structure in the Soret region.

The N_x and B_x bands of OPP-THP and bacteriochlorophyll *a* are the only spectral features we have encountered in these calculations that are affected by expansion of the CI basis set beyond that of the four orbital model. Our calculations and those of Otten (39) show that the N_x band steadily loses predicted intensity (dipole formula) to the B_x as the number of configurations is increased. When all 99 singly excited configurations are included, the predicted $\underline{N}_x$ oscillator strength drops to an entirely reasonable 0.08. (39)

Chlorin has many more allowed bands than either porphin or OPP-THP because chlorin has lost one plane of symmetry. Indeed, no band is strictly forbidden in the y direction in chlorin. The calculated ultra-violet spectrum of chlorin beyond the Soret band (Fig. 5) has many allowed bands descended from forbidden bands of the porphyrin ring. These bands usually have a predicted oscillator strength of at least 0.04, and often as much as 0.2.

The ultra-violet spectrum of OPP-THP, on the other hand, is predicted to have no electronically allowed transitions at all for 10 700 cm^{-1} above the energy of the Soret band. None of the allowed bands in this region of the porphin spectrum is predicted to be there in OPP-THP. The $\underline{L}$ band has been eliminated by the loss of a bonding orbital, the $\underline{N}_x$ band has been red-shifted below the Soret energy, and the $\underline{N}_y$ has been blue-shifted by the rise in $4e_{gy}$ orbital energy. This prediction is largely rooted in the symmetry of the molecule, and extends to bacteriochlorophyll and presumably to other substituted OPP-THP derivatives.

ASMO calculations on free base chlorin, using orbitals calculated for the metal derivative and the "$\Delta\alpha = 5.5$" parameters of McHugh, (7) indicate that the Soret band of this compound should include three major allowed electronic transitions, much as in free base porphin. (7,38)

B. Substituted Porphyrins:

To help the reader through the subsequent discussion, we have summarized our interpretation of the experimental energy level diagrams for magnesium porphyrins related to chlorophyll a in Fig. 8. Our assignments are deduced in the following sections by comparison of absorption and MCD spectra of related compounds, using the calculations judiciously as befits their fallibility as guides.

a. Protochlorophyll: Theory and Phenomenology

The experimental absorption, CD and MCD spectra of protochlorophyll a (13) are shown in Fig. 9. Assignments shown for the visible and Soret regions are those made by Houssier and Sauer. (12,13) Assignments at higher energy are by analogy to metal etioporphyrins (7) and 2,4-diacetyl deuteroporphyrins.* (56)

Results of an extensive CI, SCMO-PPP calculation of monocarbonyl porphin, intended to represent protochlorophyll a, are shown in Fig. 10, along with experimental energies and the results of a more recent calculation by Song, (41) which used a point charge to represent the central magnesium ion. Both calculations give substantially accurate predictions of the Q energies, although Song's gives the better value for

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*Deuteroporphyrin IX is 1,3,5,8-tetramethyl, 6-7-dipropionic acid porphin.

$E(\underline{Q}_x) - E(\underline{Q}_y)$. Both calculations greatly overestimate the $\underline{B}$-$\underline{Q}$ energy splitting. Our calculations predict the next states above the $\underline{Q}$ band to be the closely spaced $\underline{B}_x$ and $\underline{B}_y$ states. The Song calculation predicts three intense transitions in the same region.

The experimental Soret band of protochlorophyll a is deceptively complex. The split into $\underline{B}_x$ and $\underline{B}_y$ is clearly indicated by fluorescence polarization, (12) and is consistent with the CD and dimer absorption. Yet the $\underline{B}_x$ transition shows only a very slight negative MCD - too small to show up on the figure - and the well shaped double MCD corresponds in wavelength to the $\underline{B}_y$ and the small satellite band on the short wavelength tail of the Soret.(13,66a) In zinc deuteroporphyrin, a metal porphyrin whose Soret band should include only two degenerate transitions, there is a typical double MCD. This evidence suggests that the Song assignment could be correct, and that the double MCD could result from a near degeneracy between the $\underline{B}_y$ and a new transition just above it. Alternatively the $\underline{B}_x$ and $\underline{B}_y$ MCD may have different shapes and amplitudes. Neither of these explanations is completely satisfying.

The main effect of carbonyl substitution in our predicted absorption spectrum of monocarbonyl and 2,4-dicarbonyl porphin at higher energies is to break down the symmetry and make forbidden bands allowed. The major new feature of the spectrum is the appearance of the $(1a_{1u}2b_{1u})$ and $(3a_{2u}2b_{1u})$ bands in the spectrum at wavelengths above the Soret band, with predicted oscillator strengths of 0.13 in monocarbonyl and 0.55 in dicarbonyl porphin. Both these bands are forbidden in full square symmetry. From their energies and their prominence in the spectrum of carbonyl porphyrins, they should correspond to the η bands identified in the experimental spectra of metal 2,4-diacetyl deuteroporphyrins reported by Caughey *et al.* (*56*) In place of the *N* and *L* bands of square porphyrin, the model predicts a cluster of bands of various parentages and polarizations. These predictions are consistent with the untidy appearance of the protochlorophyll and metal 2,4-diacetyl deuteroporphyrin spectra in this region.

The absorption curve in Fig. 9 suggests that the η band is split into two components of opposite polarization, as indicated by two bumps on the absorption curve and a trough in the CD curve. The trough is much deeper in vinyl protochlorophyll,(*12*) a fact which may indicate a new pi-pi* state involving the vinyl group. Such states are predicted by SCMO calculations in which vinyl groups are introduced explicitly. (See Discussion section below.)

The *N* absorption band in protochlorophyll shows signs of three separate transitions. The first (N_1) corresponds to the 332 nm peak called *N* by Caughey *et al.* (*56*) The second (N_2)

is a slight inflection at about 325 nm, and the third ($\underline{N}_3$) appears as a shoulder in the absorption and as a peak in the CD. The L band can no doubt be further resolved as well. A new band, the M Band,(7) appears at 239 nm.

A new bonding and a new anti-bonding orbital are introduced into the pi system for each carbonyl substituent. These are not predicted to have any direct effect on the low energy spectrum; neither B nor Q transitions have any appreciable charge transfer component. n-pi* levels are not included in the present calculation.

b. Pheophytins and Other Free Base Chlorins: Phenomenology

The spectra of chlorophyll derivatives provide a useful test of the ideas developed to rationalize the spectra of unsubstituted reduced porphyrins. To facilitate comparison, we have constructed a graded series of substituted free base chlorins, each one differing only slightly from its predecessor. (MCD and quantitative absorption spectra for a comparable series of metal chlorins are not available.) The compounds used are listed in Table I; representative spectra are shown in Figs. 11 and 12.

Ideally, of course, we would like to have a set of calculations so accurate that they lead immediately to correct spectroscopic assignments. In fact, the calculations are not accurate, and contain parameters which makes them fit the data

- in a way which depends on assignments made with the help of the calculations. To avoid this circular path, we have tried to make our assignments by comparing "unknown" spectra with those of the unsubstituted parent rings, which we assume to be well understood.

Detailed comparison of the visible portions of these and other absorption spectra shows five regions whose appearance remains similar from molecule to molecule, a fact well documented by the early German spectroscopists.(69,71) The region at longest wavelengths includes a sharp, intense band, usually together with a satellite at slightly higher energy. The intense absorption band, which is associated with a small positive MCD peak, is assigned to the Q_y transition. The second and third regions contain low humps from 540-590 nm (550-615 nm in pyromethyl pheophorbide). The fourth peak at 536 nm in pyromethyl pheophorbide is clearly assigned to the Q_x transition by the large negative peak in MCD (Fig. 11) and the small positive CD band. This confirms the earlier assignment, which was based on the well-resolved negative peak in the fluorescence polarization (25) of pheophytin *a*, whose absorption spectrum is practically the same as that of pyromethyl pheophorbide *a*. The same peak appears at 519 nm in the absorption spectrum of etiochlorin (Fig. 11).

Turning now to the spectrum of unsubstituted free base chlorin in Fig. 11, we see that this peak is absent. We interpret this to mean that the (0-0) band of the $\underline{Q}_x$ transition has no intensity - i.e., that the transition dipoles of the configurations making up the $\underline{Q}_x$ state have cancelled exactly. This proposal needs to be confirmed by MCD. If it is correct, this transition will be a convenient point to calibrate parameters for future calculations on free base chlorins and pheophytins.

All six of the spectra in figures 11-12 show a fifth band at 480 nm, which apparently corresponds to the transition recently identified by McHugh et al in free base porphins (7). The band does not show up clearly in the MCD (Fig. 13). It disappears in chlorophyll a and in Mg 9-oxy-desoxo methyl pheophorbide a (72), lending weight to the suggestion that it is specifically a free base transition.

The spectra of tetraphenyl-, etio-, and unsubstituted chlorins are less clear-cut. The "480" band is present in free base tetraphenyl chlorin and absent in most of its metal derivatives, but is present in the copper, silver and tin complexes.(52) Free base chlorin and etiochlorin have a prominent double peak between 488-496 nm. The low temperature fluorescence polarization spectrum of free base chlorin shows that the twin peaks are of opposite polarization (74), strongly suggesting that they are the (0-1) of the $\underline{Q}_x$ and the (0-0) of the x-polarized "480" band, respectively. On the other hand, the spectrum of Mg chlorin shows a similar band, although it is weaker and red shifted.(73) Low temperature fluorescence polarization studies of this molecule and of Mg etiochlorin might well settle the assignment in this region.

The Soret bands of the free base chlorins are complicated to interpret. The Soret band of unsubstituted free base chlorin can be resolved into two components of nearly the same energy and intensity but of opposite polarization, (74) split by only 550 cm^{-1}. These are assigned to the $\underline{B}_y$ and $\underline{B}_x$ transitions, in order of increasing energy. Nearly all of the free base chlorins listed in Table Ia and Ic show the single, well-shaped absorption band exemplified by meso-phyllochlorin in Fig. 12. This is known as a chlorin-type spectrum. The Soret band of 9-desoxo-meso-pyromethyl pheophorbide is well-shaped but is broader than that of meso-phyllochlorin. $\underline{B}_x$ and $\underline{B}_y$ are apparently degenerate in these molecules within the resolution of the spectra. We cannot exclude the possibility of an $\underline{N}_y$ transition in the short wavelength tail of the Soret band of these spectra by analogy to the Sundbom assignment for free base porphin. (38)

In meso-pyromethyl pheophorbide, the Soret band is weaker in intensity, and is split into two components of different energies and intensities. This is known as a phorbin-type spectrum. Most previous workers have assigned the main peak and the shoulder to $\underline{B}_x$ and $\underline{B}_y$ transitions, respectively, (6,17) an assignment based mostly on fluorescence polarization data. (26,70) They assumed that these transitions are degenerate in chlorin-type compounds.

This assignment is insufficient to explain the MCD spectra shown in Fig. 13. In chlorin $\underline{e}_6$, whose absorption resembles that of meso-phyllochlorin, a large positive MCD at the long wavelength of the Soret at 420 nm is followed by a huge negative peak at 395 nm. The cross-over point of the MCD lies on the long wavelength side of the absorption maximum. A large positive peak corresponds to the satellite band in absorption at 364 nm. This spectrum is consistent with a doubly degenerate $\underline{B}$ band and a vibrational overtone or new electronic transition at higher energy. This assignment, however, leaves open the question of why the upward and downward humps of the MCD are so unequal, and also why the cross-over point does not correspond to the absorption maximum, as it should for a doubly degenerate transition. (No fluorescence polarization data is available for chlorin $\underline{e}_6$.)

In the phorbin-type Soret band of pyromethyl pheophorbide, on the other hand, the upward and downward excursions of the MCD are almost equal in magnitude, and the cross-over point comes at almost exactly the same wavelength as does the absorption peak. In other words, the main peak of the "split" Soret gives the typical MCD of a doubly degenerate transition - a pattern much simpler than that associated with a "well-shaped" Soret band. Moreover, the downward excursion shows a well-defined shoulder that corresponds nicely to the shoulder on the "split" Soret band.*

We tentatively conclude that the main peak in both "split" and "well-shaped" Soret bands - i.e., both phorbin and chlorin-type spectra - comes from a doubly degenerate B transition, and that the shoulder on the "split" Soret band of pheophytins and pheophorbide is a third transition. In chlorin-type spectra, this newly identified transition is either forbidden or else buried under the intense B bands. This conclusion is implicit in the tabulated assignments of Houssier and Sauer. (13) In the absence of reliable calculations for absorption and MCD intensities, it is difficult to assign this intensity to a particular forbidden electronic band. We shall tentatively call this new transition η by analogy to the spectra of carbonyl substituted porphyrins. (56) Again, a positive MCD peak appears at wavelengths corresponding to the Soret tail.

The difference in structure between 9-desoxo-meso-pyromethyl pheophorbide a and meso-pyromethyl pheophorbide a is the carbonyl substituent on the cyclopentene ring - i.e., the conversion

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*It should be pointed out that if two positive Gaussians with nearby peaks are added, their apparent maxima are pushed closer together. If a positive and a negative Gaussian are added, the maxima will appear to be further apart than they really are.

of the cyclopentene ring into a cyclopentenone ring. This seems to be the critical requirement for a phorbin-type spectrum. Chlorin e_6, for example, with an α-saturated substituent on the *meso* position and an α-carbonyl at the 6 position, has a chlorin-type Soret peak. Introduction of the cyclopentene ring broadens the Soret band, presumably due to the new unresolved transition, and the carbonyl group splits out the resolved shoulder, reducing the intensity of the main peak.*

This new assignment is consistent with the fact that the ratio of the heights of the main peak and the shoulder of the chlorophyll *a* Soret band (which we shall later assume to be analogous to that of pheophytin) varies from 0.54-0.95 depending on the solvent. (75) We simply assume that the configuration interaction giving rise to intensity stealing by η from B is solvent (or ligand) dependent, much as it is in bacteriochlorophyll. This is admittedly arbitrary, but it seems more likely than solvent dependent configuration interaction between B_x and B_y. Alternatively, the relative extinction coefficients of B and η may change depending on the energy split between them, without any change of relative oscillator strength.

The fluorescence polarization spectrum of pheophytin *a* (17,25) shows that the red side of the main Soret peak is strongly x-polarized, while the satellite peak is polarized approximately randomly in the plane. (The data are also

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*A phorbin molecule is a chlorophyll *a* derivative with a magnesium and an isocyclic ring. (8) By this definition, 9-desoxo-*meso*-pyromethyl pheophorbide *a* is a phorbin but does not have a "phorbin-type" spectrum.

consistent with a polarization of ± 45° to the x-axis, or to a superposition of x- and y-polarized transitions.) This observation, which was the basis for the old assignment, can be made consistent with our proposed assignment if it is assumed that the B_y loses more of its intensity to the π than does the B_x. It is not clear without explicit calculation whether our assignment is consistent with the pheophytin *a* CD spectrum. The observation that the CD of the Q_x and Q_y transitions are opposite in sign cannot necessarily be extended to the Soret bands.

d. The Chlorophylls: Phenomenology

The visible spectra of the chlorophylls and their derivatives are more poorly resolved than, and hence are best assigned by comparison to, those of the pheophytins. The visible absorption spectrum of chlorophyll *a* (Fig.2,14,15) shows four humps similar to, although not as well resolved as the first four humps of the pheophytin *a* spectrum. Fluorescence polarization (25,26,70) (Fig. 14) and magnetic circular dichroism (13) (Fig. 15) show clearly that the intense peak at longest wavelength is the Q_y, while the third hump at 578 nm is the Q_x. The visible spectra of chlorophyll *d*, 2-acetyl-2-desvinyl chlorophyll *a* (14) (Fig. 3) and Mg-9-oxy-desoxo-methyl pheophorbide *a* (72) resemble that of chlorophyll *a*, as do those of a variety of allomerization intermediates. (76) We may assign the third hump in each to the Q_x. (This comes at 591 nm in 2-acetyl-2-desvinyl chlorophyll a.) The 471 nm hump in the pheophytin a spectrum is weakly x-polarized (17), and is nearly absent in chlorophyll a. This is again consistent with our tentative assignment of this band in other free base chlorins as a separate x-polarized electronic transition. The visible spectrum of chlorophyll b beyond the Q_y is almost completely structureless; fluorescence polarization measurements taken in castor oil indicate that the Q_x band is a small shoulder that appears to the red of the hump at 594 nm when the spectrum is taken in ether solution (26,17). MCD spectra for these compounds would be useful for testing these assignments.

The Soret region of chlorophyll a in ether (Fig. 15) shows an intense peak at 428 nm (in ether) accompanied by a satellite band at higher energy. It thus resembles the phorbin-type "split Soret" of the pheophytins. As in the pheophytins, the main peak and its satellite have been assigned by previous workers to the B_x and B_y transitions from fluorescence polarization measurements. (12,17,70)

The MCD spectrum of chlorophyll a in the Soret region (13) (Figure 15) shows a clear double MCD with a cross-over precisely at the absorption maximum, much like that of the pheophytins. A shoulder on the MCD at 398 nm corresponds fairly well to the absorption shoulder at 409 nm. (See footnote, p.31.) In contrast to previous workers but in agreement with our remarks on pheophytins, we assign the main peak to a doubly degenerate *B* and the hump at higher energies to a band, forbidden in unsubstituted chlorin, which steals intensity from the Soret because of the distortion of the chlorin pi system by the isocyclic ring and its conjugated carbonyl.

This intensity stealing is responsible for the observation that phorbin-type Soret bands are less intense than chlorin bands, both absolutely and relative to the intensity of the visible transitions. MO calculations suggest that both this shoulder and the second shoulder at 380 nm are derived from overlapping "mongrel" (mixed parentage) bands descended from eta, *N* and forbidden porphyrin transitions. It may well be related to the hypothetical state just above the Soret state that we invoked as a possible explanation for the MCD spectrum of protochlorophyll *a*. We shall, for convenience, label the two chlorophyll *a* shoulders η_1 and η_2 by analogy to the protochlorophyll *a* spectrum. The broad absorption between 325-380 may well conceal further structure and new electronic transitions made slightly allowed by the reduction of the ring. The shallow hump at 325 nm in the chlorophyll *a* spectrum corresponds nicely in energy and shape to the protochlorophyll N_1 band.*

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*Gurinovitch *et al* (18) have suggested that this peak may be related to the $n\pi^*$ transition observed in cyclopentanone. (77) We regard this as unlikely, since $n\pi^*$ bands have little intensity and the 325 nm transition appears in many porphyrins.(56)

As in pheophytin *a*, this assignment can be made consistent with the fluorescence polarization data of Figure 14 if we assume that the B_y transition loses more of its intensity to the η_1 than does the B_x. This would account for the x-polarization of the red side of the main Soret peak. The first shoulder is practically unpolarized. (Fig. 14) The second shoulder, which we have labeled η_2, has a slight y polarization. The third hump, which we have called *N*, is an envelope of many bands. Our proposed assignments for the chlorophyll *a* spectrum are shown in Figure 15.

Qualitative absorption spectra by Holt (72,76) make it possible to construct a graded series of magnesium chlorins parallel to the series of pheophytins discussed in the previous section. The Soret band of phyllin e_6, (76) the Mg derivative of chlorin e_6, is a narrow single "chlorin-type" peak with a vibrational shoulder much like that of chlorin e_6. So is that of Mg 10-oxy-desoxo-methyl pheophorbide. (72) The latter compound, in which the chlorophyll *a* isocyclic cyclopentenone ring has been reduced to a hydroxy-substituted cyclopentene ring, has a Soret band much narrower than that of its free base.

In the allomerization intermediate Mg purpurin-7-lactone methyl ether dimethyl ester, the five-membered isocyclic ring is converted into a substituted six-membered lactone ring (Table I(d)). The Soret band is broader than that of the above two compounds, but does not have a resolved η shoulder. (76) These spectra are consistent with the idea that the η shoulder is resolved only in the presence of a carbonyl substituted, five-membered isocyclic ring. In view of the solvent effects on the intensity ratio of B and η transitions of chlorophyll a, (76) it would be well to check for solvent effects in the Soret region of these spectra as well.

The addition of a second carbonyl group complicates the Soret region in ways that we cannot interpret in detail. Chlorophyll b and its pheophytin have chlorin type spectra. (41) The chlorophyll d and 2-desvinyl-2-acetyl chlorophyll a Soret spectra are probably related to the phorbin spectrum (Fig. 3). The first Soret shoulder (η_1) has moved closer to the main peak, giving a lumpy appearance to the band. The secondary peak at 382 nm is the η_2. (Chlorophyll c is a porphin, not a chlorin. (79))

Mg purpurin 18 methyl ester (76), in which the isocyclic ring is a six-membered anhydride ring, has a pronounced Soret shoulder. The Soret band of Mg purpurin 7 trimethyl ester (76) appears to contain three closely spaced peaks. (See Table I(d) and I(a) for structures.) In this compound, there is no isocyclic ring at all. Apparently a carbonyl substituent conjugated to the γ position is sufficient to complicate the Soret band by itself.

Visible and Soret absorption spectra of the pheophytin *a* and *b* derivatives of zinc, copper (+2), and nickel (+2) are similar to those of chlorophyll *a* except for small shifts and changes in intensity. (79) Jones *et al* (80) report a broad transition at higher energies than, and well resolved from the Soret band of copper pheophytin *a* but not of zinc pheophytin *a*. The intensity of the η_1 band thus appears to be a function of the central metal. The manganous pheophytin *a* (81) spectrum resembles that of chlorophyll *a*.

Loach (81,82) has prepared pheophytin *a* derivatives of manganic manganese and of ferric and ferrous iron. The spectra show a weak absorption in the visible and an intense Soret band, but otherwise are different from the typical chlorin or phorbin spectrum. Apparently the ring pi-pi* transitions overlap and interact with charge transfer transitions involving both ring and metal, much as they do *in* manganic porphyrins (83) and in hemins. (84,85)

It would be useful to have MCD spectra of all of these compounds, as well as absorption spectra of the free bases of the allomerization intermediates discussed in the last paragraph. The near infra-red absorption spectra of manganic pheophytin *a* would also be of interest, since Baker (86) has recently identified crystal field transitions in the weak near IR absorption spectra of manganic hematoporphyrin. It goes without saying that all our assignments are tentative, the more so since the art of interpretation of MCD spectra is still in its infancy.

There remains to be discussed the fluorescence polarization spectrum of zinc tetraphenyl chlorin and of chlorophyll a in frozen alcohol glass. (87) In these molecules, the third visible transition at about 575 nm, which we have identified as the $\underline{Q}_x$ band in the spectrum of chlorophyll a in ether, almost disappears. The nearest thing to an x-polarized transition that remains is a band at 639 nm in chlorophyll a (~ 600 nm in zinc tetraphenyl chlorin), which Sevchenko et al (88) identify as a shifted $\underline{Q}_x$. We prefer to believe that these bands are the (0-1) overtones of the $\underline{Q}_y$, which in chlorophyll a are unpolarized (in contrast to the strongly y-polarized (0-0)) and have a slightly negative MCD. In other words, we believe that the $\underline{Q}_x$ under these conditions is greatly reduced in intensity. CD and MCD spectra would again be useful in helping us choose between these interpretations.

The bacteriochlorophyll a Soret band shown in Figure 7 varies greatly with solvent and cannot be analyzed with a simple model. We believe that there are at least five transitions between 310-410 nm, although only three are indicated on the diagram in Fig. 8. MCD (63) and fluorescence polarization (17,88) spectra show clearly that the main peak at 357-373 nm and its major long wavelength shoulder at 390-400 nm are the

B_x and B_y, respectively. There is a shoulder at 406 nm in the ether spectrum, which we shall call "B^-". and a definite inflection ("B^+") between the two *B* daughters which appears in all four solvents in absorption and/or MCD.

A fourth and fifth band at 339 and 317 nm in bacteriochlorophyll vary greatly in intensity from solvent to solvent. We shall call them η_1 and η_2, respectively. We should point out that some of these complications may be due to the simultaneous presence of several solvated species. The absorption of bacteriopheophytin *a* in ether generally resembles that of bacteriochlorophyll. (17)

e. Reduced Porphyrins: Theory

Table II compares theoretical results on reduced porphyrins with the phenomenological assignments deduced in the last section. It also shows the theoretical results of the "electrostatic model" of Song. (41,66)

The calculations reproduce the visible energies and intensities of the chlorins rather well, raising the hope that the wave functions for these states may be useful in calculating the effects of intermolecular interactions on the spectrum in this region. The calculations on substituted porphyrins, like those on unsubstituted rings, overestimate the *B*-*Q* energy split and do not treat central metal or saturated substituents explicitly. This makes it difficult to see how well we have represented the effects of individual substituent perturbations.

For this reason, we selected pairs of chlorin free bases from the graded series described earlier and compared the experimental effects of simple substitutions with the results of calculations meant to simulate them (Table III). As the spectra in Fig. 11-12 show, both 2-vinyl and 6-carbonyl substitution produce a marked red shift in B and Q energies. Of the four possible quantitative comparisons of theory and experiment, two agree reasonably well, one disagrees, and one is moot for want of sufficient data. Predictions of substituent effects on intensity are less successful in part because the experimental effects themselves are inconsistent from compound to compound. Many of the experimental substituent effects in Table III are not treated in the present calculation, but are included as an aid to future theoreticians.

The spectra of Fig. 12 and the experimental data in Table III show that the closing of the isocyclic ring dramatically increases the intensity of the Q_x but not that of the Q_y. Djerassi (9) has pointed out that the intensity of the Q_x band in a similar series of free base chlorins is especially sensitive to substituents. This behavior parallels that of the porphyrin Q band, and is characteristic of transitions which are "parity forbidden" because of a cancellation of transition dipoles due to configuration interaction. A small perturbation can change the CI coefficients of the Q_x enough that the transition dipoles no longer cancel, and can thus produce large relative changes in intensity. The transition dipoles of the configurations making up the chlorin Q_y are not near cancellation, with the result that this band is insensitive to the influence of substituents. Explicit calculations of the effect of isocyclic ring closure on chlorin ring geometry predict a 2- to 3-fold increase in Q_x intensity, and little or no change in Q_y.

The predicted Soret oscillator strength is greatly overestimated by the transition dipole formula; transition gradients (Fig. 5) do much better, at least on unsubstituted porphyrins. (7) Our calculations predict a very small splitting in the Soret region between B_x and B_y transitions, in agreement with our independently deduced assignments. The spectrum predicted by our regular parameters has only weak bands at energies higher than the Soret. This disagrees with our assignment of the Soret satellite to a new electronic transition.*

To explore the reasons for this latter disagreement, we have introduced for oxygen the parameters of Tichý et al, (50) which increase the conjugation between the carbonyl and the ring. We have used the newly available geometry of methyl pheophorbide a (49) to represent the distortion of the pi system

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*Since the completion of this manuscript, Knox (91) has done SCMO-CI calculations in excellent agreement with our assignment.

by the isocyclic ring. Each of these changes has the effect of increasing the predicted intensity of a y-polarized transition just above the Soret band. Together they raise the oscillator strength of this transition and lower that of the $\underline{B}_y$ until their ratio reaches 0.45. This result would be consistent with the fluorescence polarization data shown in Fig. 14. It would be interesting to repeat these calculations with more configuration interaction. The "electrostatic" model of Song (41) also predicts three separate electronic transitions in the Soret band region. However, the lowest of these in energy is polarized parallel to the emitting transition, in clear disagreement with experiment.

The calculated shape of the chlorophyll a Soret band is thus sensitive to the choice of theoretical parameters within the intrinsic uncertainty of these parameters. We therefore cannot appeal to the theory to decide between competing assignments. There is as yet no theoretical treatment of the vibronic interactions between the Soret band and the electronic transitions close to it in energy. We conclude that our proposal, that the Soret satellite of chlorophyll a is actually a new electronic transition not treated by the four-orbital model, is consistent with the data and is not excluded by the calculations.

Song (41,66) has performed SCMO calculations on chlorophylls a, b and d, including explicit representation of saturated substituents. He tried four different sets of semi-empirical parameters, and selected as the one most nearly in agreement with experiment a set which represents the central magnesium ion as a point charge of +1.5 electrons that affects the ionization potentials and electron repulsion integrals of the nitrogens. This is in disagreement with theoretical work by Zerner and Gouterman,(92) which indicates that the charge on the magnesium is +0.6. Still, no careful theoretical study has been made of the effects of metal charge on porphyrin spectra, and Song's assumptions -- which amount to a revision of nitrogen parameters that are arbitrary anyhow -- should be judged by their usefulness in explaining the data. The Song calculations predict the Q_x-Q_y splitting better than those of the present work, just as they do for protochlorophyll. According to his results, three allowed transitions underlie the Soret band of chlorophyll a and b, with the chlorophyll b bands spread to both higher and lower energies. Four allowed transitions underlie the Soret band of chlorophyll d; the band with the highest energy is considerably to the blue of the chlorophyll a Soret band energy.

These predictions are easy to check by MCD or fluorescence polarization, since the predicted polarizations alternate in each molecule between parallel and perpendicular. The experimental chlorophyll *a* polarizations discussed earlier are clearly inconsistent with his interpretation. So is the absence of an intense η shoulder in the chlorophyll *b* absorption. The Song calculations do, however, agree nicely with the absorption spectrum of chlorophyll *d*; MCD and fluorescence polarization data on this molecule would be welcome.

Our predicted energies of bacteriochlorophyll and bacteriochlorin visible bands agree reasonably well with experiment, as do those of Otten (*39*) The predicted Q_y intensities from the transition dipole formula are 2-3 times too large; those from transition gradients (Fig. 5) are too small. The Song prediction of x-y splittings in *B* and *Q* bands is very good in both bacteriochlorophyll and chlorophyll *a*.

The Soret band of bacteriochlorophyll *a* resists definitive assignment. Our calculations and Otten's predict an x-polarized shoulder on the long wavelength edge, the predicted intensity of which decreases with increasing configuration interaction. There is also a forbidden band on either side of the B_x. The calculation of Song predicts a very weak y-allowed band on the long wavelength shoulder of the B_x, and an additional weak y-allowed transition between B_x and B_y. Neither of these predictions corresponds exactly to the spectrum observed, but either could be made to fit by *ad hoc* assumptions regarding solvent-dependent vibronic interactions. Both experimental and theoretical work is needed on the solvent effects.

The Soret band of bacteriochlorophyll should be a sensitive probe of its environment even in the absence of dimerization. However, the effects of dimerization on the shape of this band will probably be too complicated to interpret in detail. Fortunately, detailed structural information can in principle be extracted from the well-resolved $\underline{Q}_x$ and $\underline{Q}_y$ transitions. (43) The predicted polarizations of the $\underline{B}$ and $\underline{Q}$ bands are shown in Table II. The $\underline{Q}$ bands of protoporphyrin (not tabulated), chlorophyll a, and bacteriochlorophyll are nearly along the symmetry axes, in qualitative agreement with fluorescence polarization experiments. In protochlorophyll a (Fig. 9), our calculation produces the curious result that both of the visible transitions are predicted to be almost parallel, i.e., $\underline{Q}_{"x"} \parallel \underline{Q}_{"y"}$. This result is contrary to the fluorescence polarization and MCD measurements of Houssier and Sauer, (12,13) which show the bands to be roughly perpendicular.

C. Other Theoretical Results

a. Triplet States

Table IV shows the predicted energies of the four lowest triplet configurations relative to the ground singlet. Group theory dictates that these configurations not interact with each other in square porphins. An extensive CI calculation

(6) indicates that interaction with higher states is not serious in these compounds. We assume that both properties carry over to the chlorophylls.

Predicted triplet energies change little from porphin to chlorin; the lowest two triplet configurations are much the same in ADJ-THP as well. In OPP-THP and bacteriochlorophyll, the lowest predicted triplet is only 5500-7100 cm^{-1} above the ground singlet. The habitual overestimation by the SCMO-PPP method of the two-electron terms that split singlet and triplet configurations means that this prediction may be too low by a few thousand wave numbers. Even so, the low-lying triplet should provide a highly favorable route for radiationless loss of excitation energy that reaches the triplet manifold, and hence a very low phosphorescence yield.

Available data on the lowest triplet energies of porphyrins related to chlorophyll a are displayed in Fig. 8. To our knowledge, no phosphorescence data is available for protochlorophyll. The lowest triplet of chlorophyll a in polar glasses emits at 11 300 cm^{-1}, close to the predicted value. (93) The phosphorescence observed from chlorophyll a in dry non-polar glasses, (94) once attributed to an $n-\pi^*$ triplet, is probably due to an aggregate. (18) To the author's knowledge, no phosphorescence has ever been reported for bacteriochlorophyll, in agreement with the prediction. Shortlived triplet-triplet absorption spectra have been observed, (95) and may well derive from a triplet state other than the lowest.

Triplet-triplet absorption spectra of metal porphin have been calculated using the traditional parameters used in this work, and were in excellent qualitative agreement with experiment. (6) The spectra are broad and relatively structureless because of the many low-lying transitions made possible by the excitation of an electron from a bonding to an anti-bonding orbital. The electron in one of the closely packed anti-bonding orbitals can be further excited to higher levels, while the "hole" in the equally closely packed bonding orbitals can be excited downward if it is filled by an electron from a lower bonding orbital. A similar situation obtains in porphyrin radical anions and cations, (30,31,39) except that these species have either the hole or the anti-bonding electron but not both. Experimental triplet-triplet absorption spectra have been measured for chlorophyll *a*, (96) and measurement of the absorption spectrum of the lowest excited singlet state of chlorophyll *a* should now be possible. (97) No calculations have been reported on the triplet-triplet or excited-singlet-to-doubly-excited-singlet spectrum of any chlorophyll.

b. Transition Monopoles

Transition monopoles are a quantitative expression of the fact that the oscillating charges ("transition density") associated with a quantum mechanical transition are inadequately represented as a point dipole, and really extend over the entire molecule. (98) The calculated transition monopoles for the Q bands of bacteriochlorophyll a are shown in Fig. 16, as derived from a calculation of 2,6-dicarbonyl-OPP-THP. These values have been normalized to agree with the experimental values of the transition dipoles for use in the calculation of intermolecular properties. The unusual solvent sensitivity of the Q_x (orange) band of bacteriochlorophyll is probably connected with the high value of the normalized transition monopole at the meso carbon and at the nitrogens of the reduced rings.

Transition monopoles from our calculations, together with certain assumptions about the conformation of ring substituents, have given reasonable values in coupled oscillator calculations of the rotatory power of the visible circular dichroism spectra of protochlorophyll a, chlorophyll a, and bacteriochlorophyll a. (99) Calculations using point transition dipoles greatly underestimated these quantities. This is not necessarily a tribute to the accuracy of our monopoles; it may be that even the crudest representation of the transition density extended over the whole molecule suffices to greatly improve the calculated interaction.

It should be possible to use these monopoles to refine earlier point-dipole calculations of the interaction between transition moments in dimers of various geometries. (43) One may further hope to use them to predict the structure of the bacteriochlorophyll trimer, which Sauer has found to be the active site of the chromatophore of the photosynthetic bacterium *Rhodopseudomonas spheroides*. (100)

The details of the structure of the chlorophyll aggregate at the reaction center of the photosynthetic unit may well turn out to be important to the mechanism of energy storage. The reaction centers of Photosystems I and II of green plants and algae, for example, are both thought to be composed of molecules of chlorophyll *a*, yet their redox potentials differ by half a volt. (101) It is also attractive to suppose that the primary photosynthetic electron donors and acceptors are so placed as to optimize the probability of hole and electron transfer, respectively, from the excited chlorophyll of the reaction center. Excited state wave functions calculated by this or similar methods could be used to suggest possible models of trap geometries -- especially after the chemical identities of donor and acceptor are known.

c. Ground State Properties

Ground state change densities and bond orders for unsubstituted reduced porphyrins are discussed in ref. 6. Knop and Fuhrhop (42) performed similar SCMO calculations and critically compared their calculated π-electron densities, free valences, and frontier orbital densities for porphin, chlorin, bacteriochlorin and phlorin, with the considerable chemical data that have only recently become available.

The effects of carbonyl substitution on the predicted ground state properties of porphyrins are exemplified by the molecular diagram of chlorophyll a in Fig. 17. A build-up of electron density on the meso carbon nearest the reduced ring is observed in this calculation and in all MO calculations of reduced porphyrins, in agreement with experiment. (6,41,102) This effect is intensified in bacteriochlorins, in which each meso carbon is adjacent to two reduced rings, again in agreement with experiment. (40,103) It is experimentally absent from free base pheophytins. (40) We also predict that the β-carbons on the half of the porphyrin ring towards the reduced pyrrole ring are strongly electrophilic, in agreement with other calculations. (6,41)

The major effect of carbonyl substitution is to shift electron density within the substituted pyrrole ring towards the carbon bearing the substituent from the carbon adjacent to the substituted carbon. Other pyrrole rings are almost unaffected. This would predict that carbonyl substituents favor nucleophilic attack on the carbons adjacent to the substituted carbon, by analogy to the familiar directive effect of aromatic carbonyl substituents.

This effect is enormously greater in the Song calculations (41) than in ours, including those of our calculations which we intended to exaggerate the effect of the isocyclic ring. Song, moreover, finds a similar shift in electron density within the vinyl substituted ring, and a strongly electrophilic β-carbon in ring II (the ring opposite the reduced ring), both in contrast with our results.

In addition, electron density is shifted in our calculations towards the carbonyl substituted ring from all four of the central nitrogens. This is consistent with the finding of Caughey that the CO stretching frequency of carbon monoxide ligated to carbonyl substituted hemes (ferrous porphyrins) increases with carbonyl substitution, while the binding constant of pyridine to nickel porphyrins decreases. (104) In each case, carbonyl substitution withdraws electrons from the center of the ring. In the first case, this makes the iron a poorer pi donor and weakens the metal-carbon bond. This increases the triple bond character of the CO band and increases the CO stretching frequency. In the latter case, electron withdrawal makes the nickel a better σ-acceptor and hence strengthens the binding between it and pyridine. While the present calculations do not treat the metal-nitrogen bond explicitly, both of these experimental results are consistent with a decrease in electron density on the central nitrogens with carbonyl substitution.

A distortion in molecular geometry intended to simulate the effect of the isocyclic ring on the pi system predicted a small increase in electron density at the δ-position at the expense of the γ. (See Table I for notation.) Distortion also produces a small increase in electron density at the center nitrogens, a fact which may explain the relative ease of protonation of chlorins containing an isocyclic ring. (18)

The bond orders of substituted reduced porphyrins predict substantial distortions in bond lengths compared to the parent porphyrin. Taking as a rule of thumb that a change of 0.1 units of bond order corresponds to a change of 0.02 Å in bond length, (2) we estimate that the CC bond linking the meso carbon to the alpha carbon of the reduced pyrrole ring will be 0.04 Å shorter than its mirror image adjacent to the unreduced ring, other things being equal. Such a distortion might induce a deviation from planarity (see Ref. 46). Quantitative predictions of any distortions would require a model for the response of sigma and pi systems to out-of-plane deformation, as well as a self-consistent treatment of the effects of distortions along various normal modes on the pi bond orders. While the porphyrin geometry predicted by our parameters is much inferior to that given by those of Sundbom, (38) this should not affect qualitative predictions regarding distortions. The only X-ray structure that has been determined for a reduced porphyrin is that of methyl pheophorbide a.(49) In this molecule, the distortions due to the isocyclic ring are much more important than those due to ring reduction.

The ground state pi dipole moment of unsubstituted chlorin is predicted to be 0.82 electron-Å in the direction towards the reduced ring. In chlorophyll a, (2-vinyl-6-carbonyl chlorin) the predicted dipole moment is 4 electron-Å toward the ring bearing the carbonyl with a slight tilt toward the reduced ring. Roughly speaking, this is the resultant of the dipole moment due to displacement of electron density towards the carbonyl group. These values are expected to be too high.

The Q excited singlet state of chlorophyll a is predicted to have a dipole moment of 3.97 electron-Å, oriented at an angle of 5 degrees from the permanent ground state dipole. This is the lowest excited singlet band of chlorophyll a, and is presumably the photochemically active excited state in photosynthesis. Bacteriochlorophyll is predicted to have no pi dipole moment in either ground or excited states. None of these moments have been measured; experimental values would be very useful in helping calibrate the model.

d. Highest Occupied and Lowest Empty Orbitals

Fig. 18 shows the coefficients of the highest occupied and lowest empty orbitals (HOMO and LEMO) of calculations representing chlorophyll a and bacteriochlorophyll a. These and analogous data show that the vinyl and carbonyl groups play little role in the excitation corresponding to the Q bands of carbonyl substituted porphyrins. This means these transitions have little "charge transfer character". Calculations using parameters that increase the conjugation of the oxygen with the ring confirm this conclusion.

The low electron density on the α-carbon of the vinyl group of chlorophyll a in the lowest empty molecular orbital raises the possibility that the chlorophyll a radical anion will have a negative spin density at this carbon. (2) The same might be true of complexes of pheophytin a with a paramagnetic metal whose odd electron can delocalize into a pi* orbital, such as Mn, Fe or Ni. Negative spin densities have already been reported for the α-carbon of the vinyl groups of cyanoprotoporphyrin IX iron (III). (105) In agreement with this observation, our calculations of the lowest antibonding orbital of divinyl porphin show coefficients on the α-carbons of the two vinyl groups of only 0.026 and -0.027.

e. Ionization Potentials and Electron Affinites

Ionization potentials and electron affinities from these calculations are shown in Table V. By Koopman's Theorem, these quantities should simply be equal to the energies of the highest filled and lowest unfilled orbitals, respectively. The predicted values are subject to a known constant systematic error due to the neglect of penetration integrals in the calculation, (106) so that only relative values are meaningful.

Examination of Table V shows that chlorins are predicted to have ionization potential within 0.05 eV of those of porphyrins, and 0.08-0.13 eV higher electron affinity. OPP-THP, on the other hand, has 0.34 eV lower predicted ionization potential than porphyrin and 0.35 eV lower predicted electron affinity. (6) The main new result of these calculations is that each carbonyl substituent raises the predicted ionization potential of a porphyrin or reduced porphyrin by 0.10-0.16 eV. It raises the electron affinity by 0.10 - 0.25 eV.

Experimentally, the midpoint potentials for one-electron oxidation of a series of metal octaethyl chlorins are about 300 mV lower than those of the analogous metal porphyrins. (107) Similarly, bacteriochlorophyll has a midpoint potential about 300 mV lower than chlorophyll a. (108) Data on work functions of porphyrins (109) are insufficient for this kind of comparison.

Discussion

The Gouterman four-orbital model emerges from this discussion as a reasonably reliable guide to the (0-0) visible bands of the chlorophylls. While the model was originally recommended for the Soret band on the basis of its success with metal porphin, chlorin and tetrabenzoporphin, (6,3) it now appears that these molecules were special cases. In particular, more configurations must be included in theoretical treatments of metal phthalocyanines, (7) of free base porphyrins at all levels of reduction, (7,38) as well as of OPP-tetrahydroporphyrins and chlorophyll derivatives with isocyclic cyclopentenone rings.

Closer examination of the experimental data on which the four-orbital model is based has revealed important second-order discrepancies. Neither the sum of the oscillator strengths of the B and Q transitions nor the B-Q energy splitting are accurately constant from molecule to molecule contrary to the model. The oscillator strength of the Q_y (red) band in chlorophyll a is nearly that of the corresponding (near IR) band of bacteriochlorophyll a, despite the prediction that it should be less.

The calculations reported here were not intended to give quantitative agreement with energies or intensities, but to guide qualitative assignments of the spectra of a family of related molecules. The π-electron theory and semi-empirical parameters were originally chosen in 1963 to guide a survey of a large number of porphyrins at a time when so complex a calculation had not been attempted.

These "standard" and "traditional" parameters have been used in a wide variety of calculations for eight years. They have done yeoman service in guiding the development of phenomenological assignments of porphyrin spectra, but it is time to work out a better treatment that will repair their obvious deficiencies. They predict a porphyrin geometry inferior to that given by the simplest valence band treatment, they badly overestimate two-electron repulsion integrals, and slightly overestimate the center of gravity between B and Q states.

What is more, there is still no satisfactory semi-empirical theory of substituent effects on the (0-0) electronic energy levels or absorption intensities, on the vibronic borrowing from the Soret band - the mechanism by which nearly all visible and for ultra-violet absorption intensity is acquired -- or of the MCD spectra of porphyrins lacking square symmetry. There is also no theory of line widths in solution sufficiently reliable to guide assignments of experimental absorption bands.

Even if we restrict our attention to the (0-0) bands, it is hard to say in advance how many of the deficiencies of this calculation can be remedied without explicit consideration of sigma electrons. One of the most important of these deficiencies is the neglect of the effect of saturated substituents on the energies of the ring orbitals. The wrong prediction of the polarizations of the visible bands of carbonyl substituted porphins was probably due to the fact that the saturated substituents raise the a_{1u} orbital relative to the a_{2u}, thus lowering the energy of the $(a_{1u}e_g)$ configurations relative to the $(a_{2u}e_g)$.

The importance of the saturated substituents also stands out in a calculation of divinyl porphin, which was intended to represent the metal protoporphyrins. A new pi orbital localized on the vinyl groups appears in this molecule degenerate with the cluster of filled MO's just below the a_{1u} and a_{2u} (see Fig. 8 of reference 6), and produces a spurious pi-pi* vinyl-to-ring transition which draws off intensity from the Soret band. This would not have happened if the effects of the saturated groups on the ring orbital energies had been included. There is a small difference in the ultra-violet CD spectra of protochlorophyll _a_ and vinyl protochlorophyll _a_ (_13_) that might be due to such a vinyl-to-ring transition. It would be interesting to have the ultra-violet CD spectrum of _Chlorobium_ chlorophyll 650 or of some other desvinyl chlorophyll _a_ for a similar comparison.

The more recent pi-pi* calculations on chlorophylls by Song (41) and on porphyrins by Sundbom (11) raise some hope that we may soon expect reliable quantitative calculations of excited state properties of these molecules. Calculations of rotary strengths using our parameters were gratifyingly successful, (99) and it would be useful to have calculations of the MCD spectra as well. A new method of calculating electron correlation in large molecules, based on many-body theory, has been developed by Gutfreund and Little, (110) and may prove useful in reducing the B-Q energy splitting in future porphyrin calculations.

Before long, the purely pi electron treatments will no doubt be supplanted by all-electron calculations which will explicitly treat n-pi* and charge transfer transitions in a self-consistent framework. Our analysis indicate that such future calculations will do well to take explicit account of 1) the effects of both saturated and unsaturated substituents on the porphyrin ring, 2) the effects of the distortion of the ring geometry by the chlorophyll isocyclic ring, and to a lesser extent 3) the steric requirements and possible non-planarity of the central metal. (10) For finer effects, it may be important to use coordinates derived from x-ray studies.

Unfortunately, there will never be a single critical experiment that will test the theory once and for all. We may instead expect gradual, uneven improvement in our capacity to predict the results of particular experiments. If results of such calculations are to have the confidence of the properly skeptical biochemist, we feel it essential that they be extensively verified by the kind of experimental tests employed in this paper.* These would be greatly facilitated if certain key pieces of experimental data were available.

First of all, the newly developed technique of high resolution photoelectron spectroscopy has made it possible to measure directly the energy of individual one-electron orbitals. Experiments on reduced and substituted porphyrins should provide a crucial check on the four orbital model phenomenology outlined in the introduction to this review.

Secondly, despite the long man-years that have gone into the synthesis and spectroscopy of chlorophyll derivatives, there are still a good many useful molecules for which quantitative spectra are not in the literature to the best of the author's knowledge. These include the metal derivatives (copper and magnesium would be most useful since they would best complement existing work) of most of the free base chlorins in Table I, and those of ADJ- and OPP-tetrahydroporphyrin, octamethyl OPP-

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*Seely (111) has suggested that the prediction of the spectrum of the "phase test intermediate" would be a good additional test for an improved model.

THP (or its spectroscopic equivalent*), the free bases of compounds 9, 17 and 18 of Table I, and bacteriochlorophyll derivatives (with and without magnesium) analogous to the sequence constructed in that Table. Allomerized bacteriochlorophylls without the isocyclic ring would also be useful. (The recent synthesis of unsubstituted OPP-tetrahydroporphyrin (112) raises the hope that the spectrum of this compound will soon be available.) MCD, CD and fluorescence polarization spectra of these derivatives, as well as those of chlorophyll b, chlorophyll d, and the Chlorobium chlorophylls would be useful. Indeed, these techniques should routinely be used in the characterization of any new porphyrin derivative. It would also be useful to have the substituted porphins analogous to chlorophyll b ("protochlorophyll b") and to bacteriochlorophyll a. A study of the absorption and MCD of these molecules in the same solvent (ether or dioxane would best complement previous work) would make it possible to trace spectroscopic effects in the visible and ultra-violet to specific perturbations. Solvent effects on the Soret region would also be of interest.

Of most practical importance would be the determination of the lowest triplet energies of the various chlorophylls. Despite repeated suggestions that triplet states might play a role in photosynthesis, Figure 8 shows that very few triplets

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*Since all α-saturated substituents seem to have identical effects on porphyrin spectra, derivatives which differ only in substituents with saturated carbons alpha to the ring are deemed spectroscopically equivalent.

of this series have been located. The energy of the low-lying triplet of bacteriochlorophyll would be especially interesting.

Finally, fluorescence polarization measurements give only the relative orientation of the transition dipoles of the different excited states, not their absolute orientation relative to the molecular axis or to the permanent dipole. Experimental measurement of this absolute orientation would provide a valuable check on the accuracy of these and future wave functions. It would also be valuable to know the ground state dipole moment and polarizability, both as a check on the wave function and because many methods of fixing the orientation of transition dipoles (e.g., electric dichroism) do so relative to the permanent dipole. Once faith has been established in the calculated direction of the transition dipole, the theorist might feel more confident in his transition monopoles.

What might we expect from such improved calculations? At the very least, we may hope that the model would be able to distinguish between possible structures of a new chemical species. This capacity would be very useful to preparative chemists confronting a small amount of brightly colored material. The embarrassing fact, however, is that MO theory has not been used to assign a porphyrin structure since bacteriochlorophyll was identified as an OPP-tetrahydroporphin from the calculations of Barnard and Jackman. (113) A theoretical interpretation of band shapes and solvent effects would also be useful, but may be outside the range of the present general theory of large molecule spectroscopy.

Probably the most important potential use of quantitative models of the chlorophyll and bacteriochlorophyll spectrum would be to calculate the intermolecular interactions that determine energy transfer in concentrated solutions and in the photosynthetic apparatus. These same interactions also determine the spectroscopic changes in absorption and circular dichroism in dimers and higher aggregates related to the structure of chlorophyll *in vivo*. One may hope that more sophisticated theories, once adequately calibrated, can be extended to larger aggregates, to monolayers, crystals, and to the antenna and reaction center chlorophylls of photosynthetic bacteria, algae and green plants, and to their interactions with primary electron donors and acceptors.

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LEGENDS TO FIGURES

Fig. 1 Structures of Photosynthetic Porphyrins.

Fig. 2 Absorption spectrum of chlorophyll *a* and protochlorophyll in ether. (*12*,*13*)

Fig. 3 Absorption spectrum in acetone of bacteriochlorophyll *a* (as in Fig. 7) and 2-desvinyl-2-acetyl chlorophyll *a*. (*14*)

Fig. 4 Molecular orbital energies in porphin, chlorin, OPP-THP, and ADJ-THP. Orbitals are labeled by porphyrin symmetries.

(a) Arbitrarily adjusted Huckel calculations (*4*)

(b) SCMO-PPP calculation using "traditional" parameters (present work). The *a* orbital is part of a cluster of closely spaced orbitals. (See Fig. 8 of Ref. *6*)

Fig. 5 Results of configuration interaction calculations for porphin, chlorin and OPP-tetrahydroporphin. For each molecule, we plot the energies of the lowest configurations and of the lowest states as given by a minimum CI model (seven orbitals for OPP-THP, four for porphin and chlorin) and by interacting all configurations below a cut-off near 150 nm. Configurations are labeled by the porphyrin orbital symmetries from which the excitations are descended. Each line on the porphin diagram represents a pair of degenerate transitions, and the oscillator strength is the sum of the two. Solid lines represent dipole allowed states; dotted lines represent dipole forbidden transitions. Predicted oscillator strengths calculated from transition gradients (*7*) are given in parentheses. The axes used here are the same as those used in previous work. (The labels Q_x and Q_y of Table IV of ref. 6 were reversed through a typographical error.)

Fig. 6 (0-0) Experimental absorption levels in matched series of metal porphyrins. Note that the vertical scale is smaller than that of Fig. 5. All spectra in benzene except as noted. Numbers above state are oscillator strengths. Numbers in parentheses below state are extinction coefficients in thousands. Numbers followed by "/2" are the summed values of two degenerate transitions.

a) magnesium tetraphenyl porphin (51), tetraphenyl chlorin (52 and tetraphenyl OPP-THP (53).

b) copper chlorin (54), porphin (54), octamethyl porphin (in chlorobenzene) (55), deuteroporphyrin (in $CHCl_3$ (56)), octaethyl chlorin (55), octaethyl ADJ-THP (57). The shape of the Soret band of octaethyl ADJ-THP is not in the literature.

c) zinc tetraphenyl porphin (58), tetraphenyl chlorin (52), and tetraphenyl ADJ-THP (58).

Fig. 7 Absorption spectrum of bacteriochlorophyll a in different solvents (63).

Fig. 8 (0-0) Experimental absorption levels in a matched series of metal porphyrins related to chlorophyll a and bacteriochlorophyll. Magnesium etioporphyrin (in EPA) (64), protochlorophyll a (12), chlorophyll a (both in ether) (13), 2-desvinyl-2-acetyl chlorophyll a (in acetone) (14), bacteriochlorophyll (in acetone) (63), and hypochlorophyll (60). N band and oscillator strengths in first column are for Mg deuteroporphyrin in chloroform (56). Other notes as in Fig. 6.

Fig. 9 Absorption, circular dichroism and magnetic circular dichroism spectra of protochlorophyll a (13). (A small negative MCD at 440 nm does not appear in the drawing. (65))

Fig. 10 SCMO-PPP-CI results for carbonyl porphin. Experimental energies are those of Fig. 9. Song calculation is for protochlorophyll. (66)

Fig. 11 Visible absorption spectra of three free base chlorins.

Chlorin (54) ——————
etiochlorin (67) ....
pyromethyl pheophorbide a (54) - - - - - - - - - - -
MCD of pyromethyl pheophorbide (9) (topmost dashed curve)

Fig. 12 Absorption spectra of three free base chlorins derived from chlorophyll a. (9,67,68) Compounds are numbered 11, 7, and 12 respectively, in Table I.

Fig. 13 Magnetic circular dichroism spectra of two free base chlorins (9) in the Soret region. Units of $[\theta]_M$ are deg $mole^{-1}$ cm^3 at 41.7 kgauss.

pyromethyl pheophorbide - - - - - -
chlorin e_6 ——————

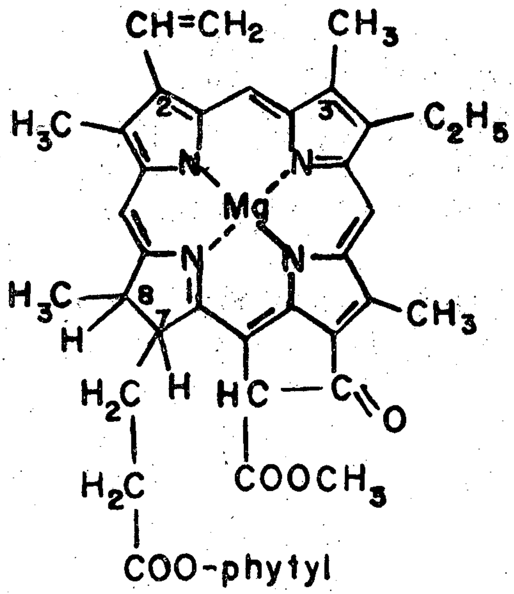
Fig. 14 Absorption and fluorescence polarization spectrum of chlorophyll a in castor oil. (70)

Fig. 15 Absorption and MCD spectra of chlorophyll a in ether. (13)

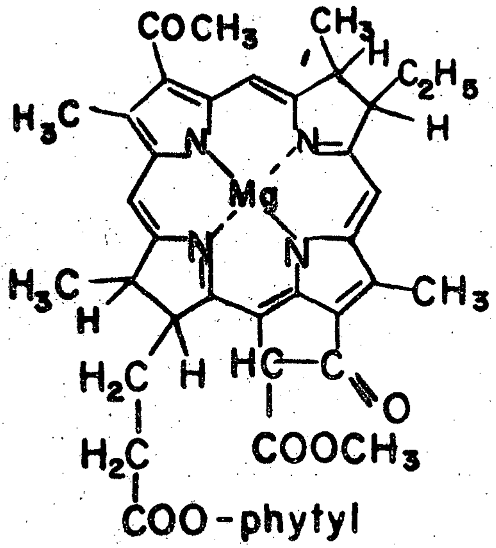
Fig. 16 Transition monopoles for near infra-red and visible Q_y and Q_x transitions in simulated bacteriochlorophyll. Monopoles are in thousandths of an electronic charge, dipoles in e-Å. All numbers are normalized to give experimental oscillator strengths when experimental energies are used. (β_{CO} = -2.36 eV, CI to 150 nm, SCMO-PPP calculations).

Fig. 17 Ground state bond orders and charge densities for simulated bacteriochlorophyll a and chlorophyll a. (β_{CO} = -2.36 eV, SCMO-PPP calculation.)

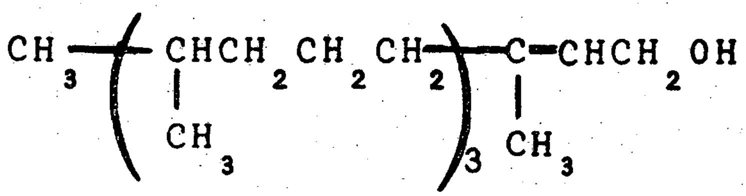
Fig. 18 Coefficients of highest occupied and lowest empty orbitals in simulated bacteriochlorophyll a and chlorophyll a. (β_{CO} = -2.36eV, SCMO-PPP calculation.) Coefficients for meso carbons are inside the ring, for α carbons outside.



Chlorophyll a
Chlorophyll b: 3-CHO
Chlorophyll d: 2-CHO
Protochlorophyll:
  7,8-dehydrochlorophyll
Pheophytin a, b, d: H_2 replaces Mg
Methyl Pheophorbide a, b, d: CH_3
  replaces phytyl in pheophytin



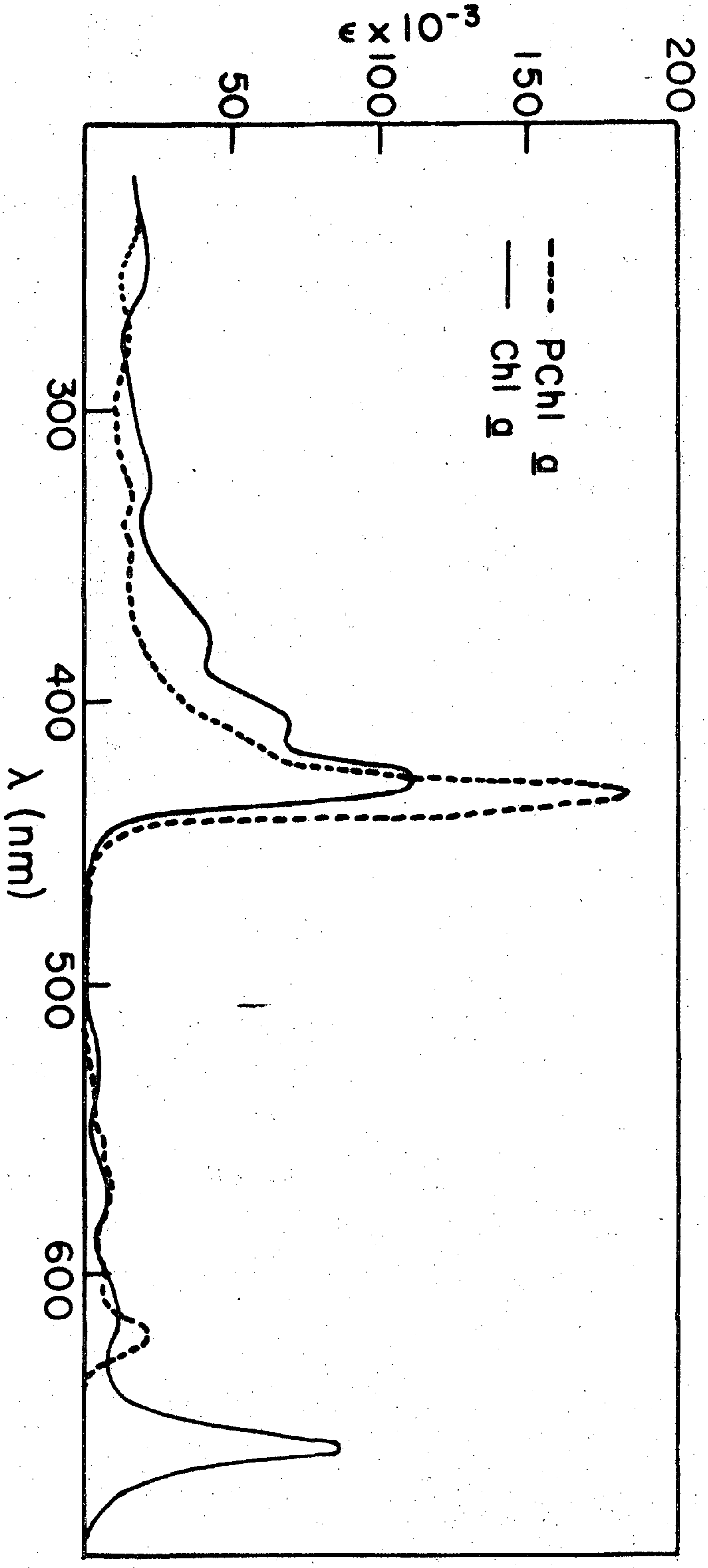
Bacteriochlorophyll



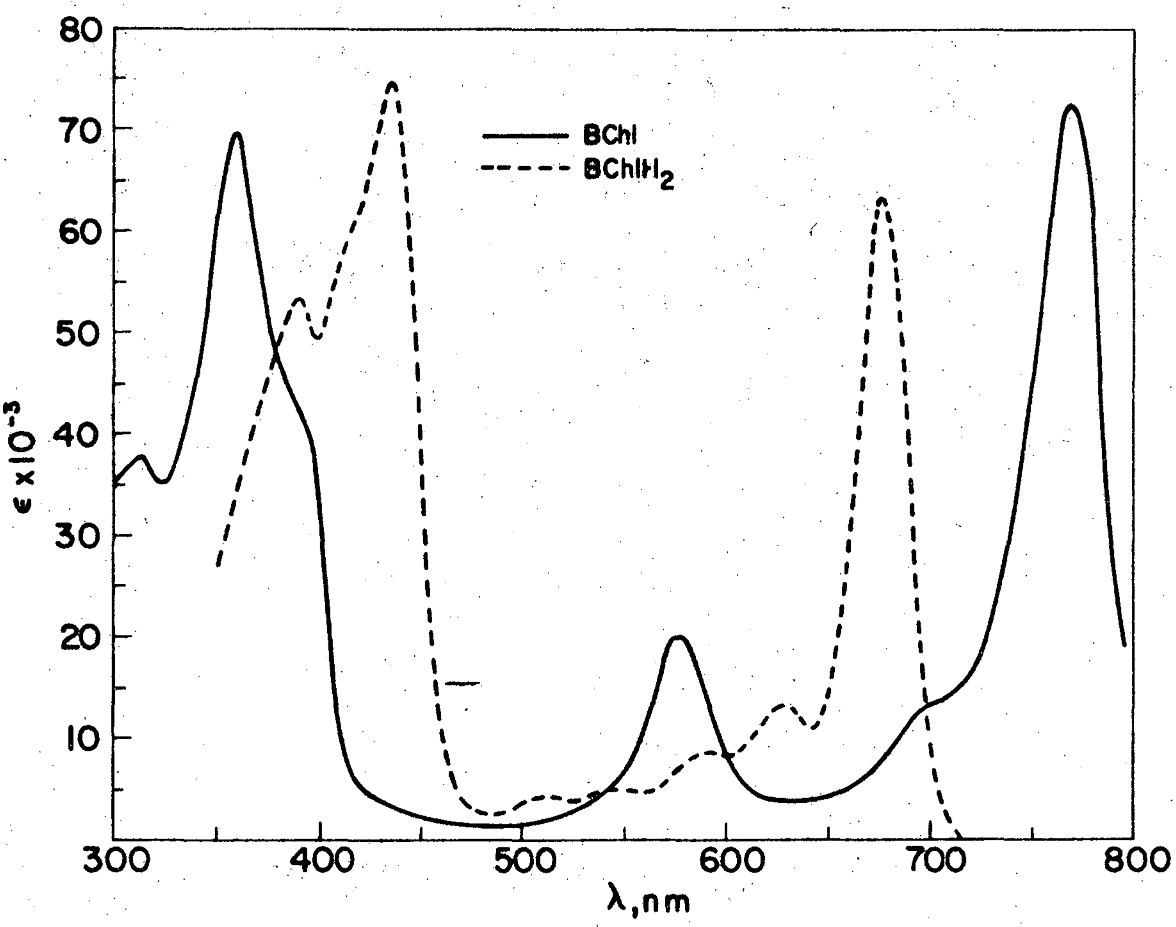
$$CH_3\left(\underset{\displaystyle CH_3}{CH}CH_2CH_2CH_2\right)_3\underset{\displaystyle CH_3}{C}{=}CHCH_2OH$$

Phytol

[illegible] Weiss Fig 1

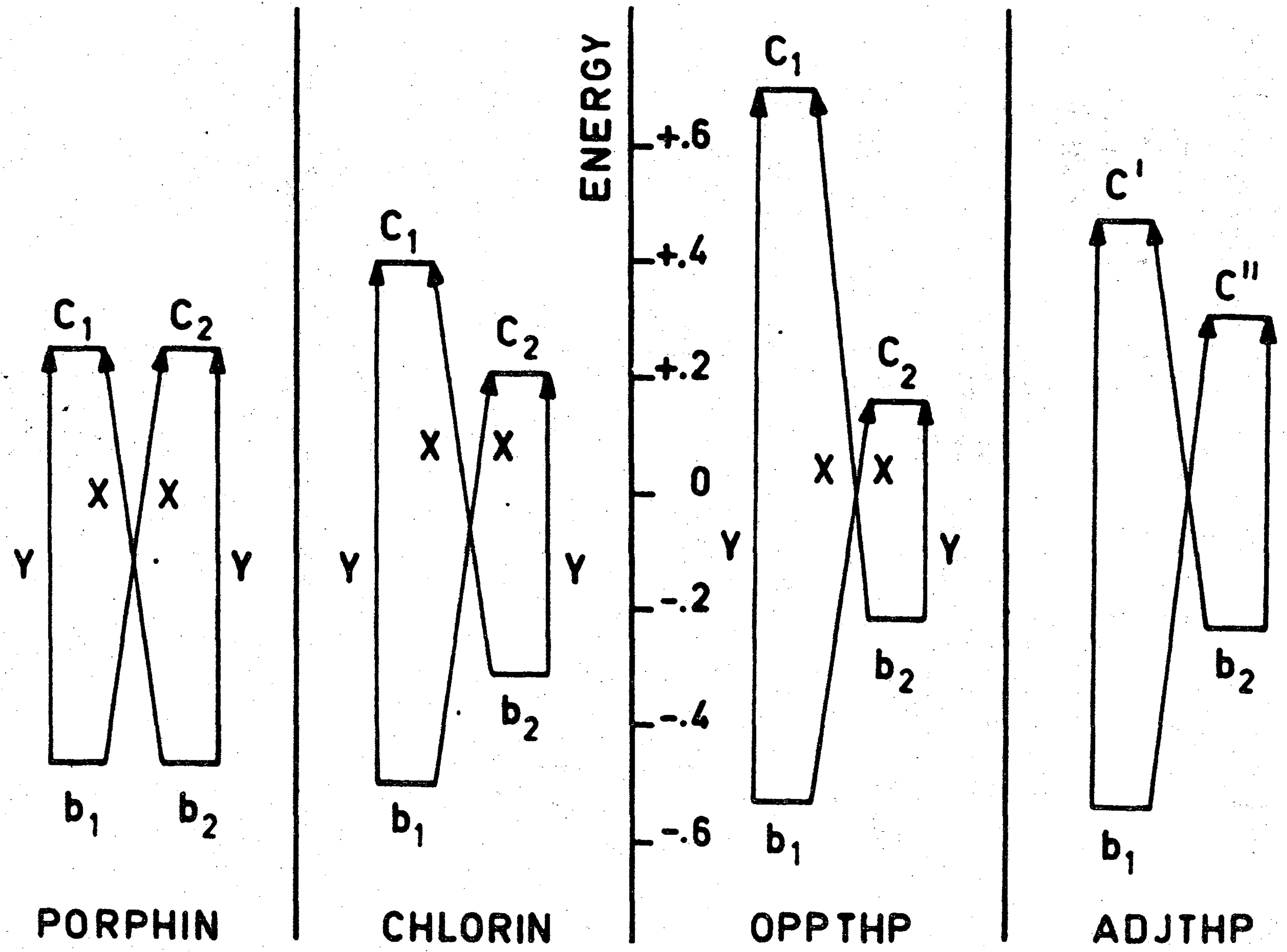


Mol Spectr.   Weiss Fig. 2

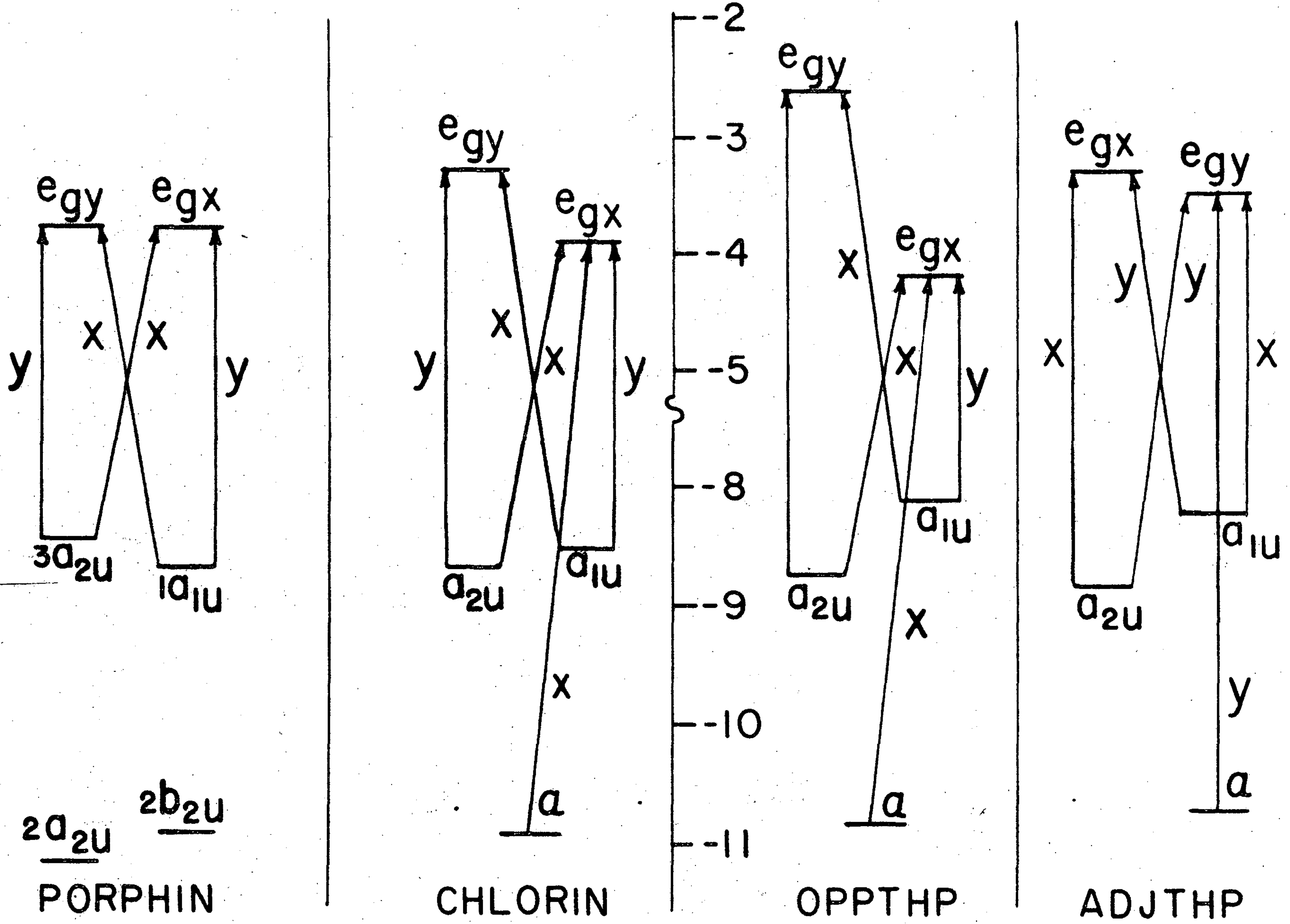


J. Mol. Spectr. Weiss Fig. 3

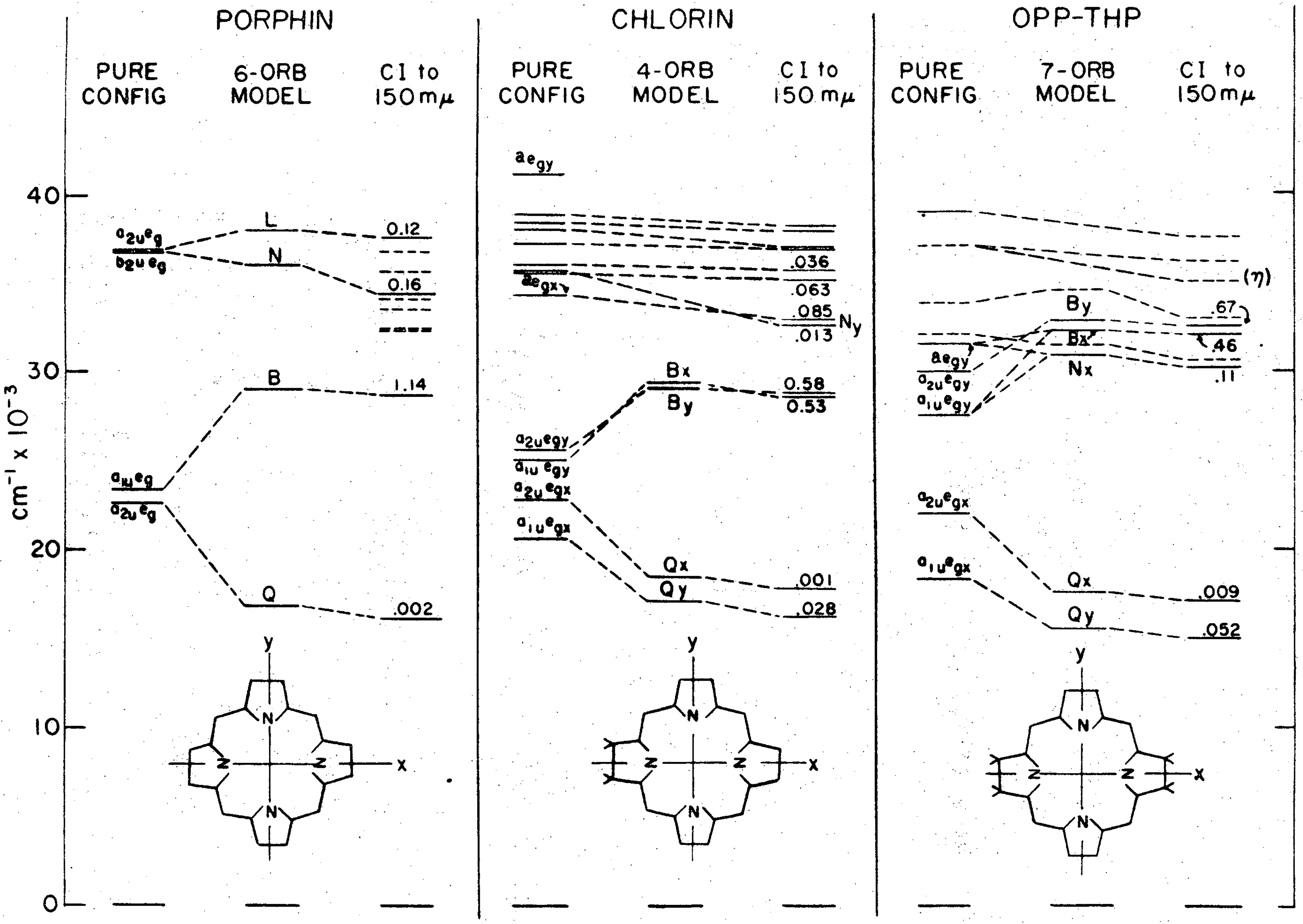
[illegible] Fig VA

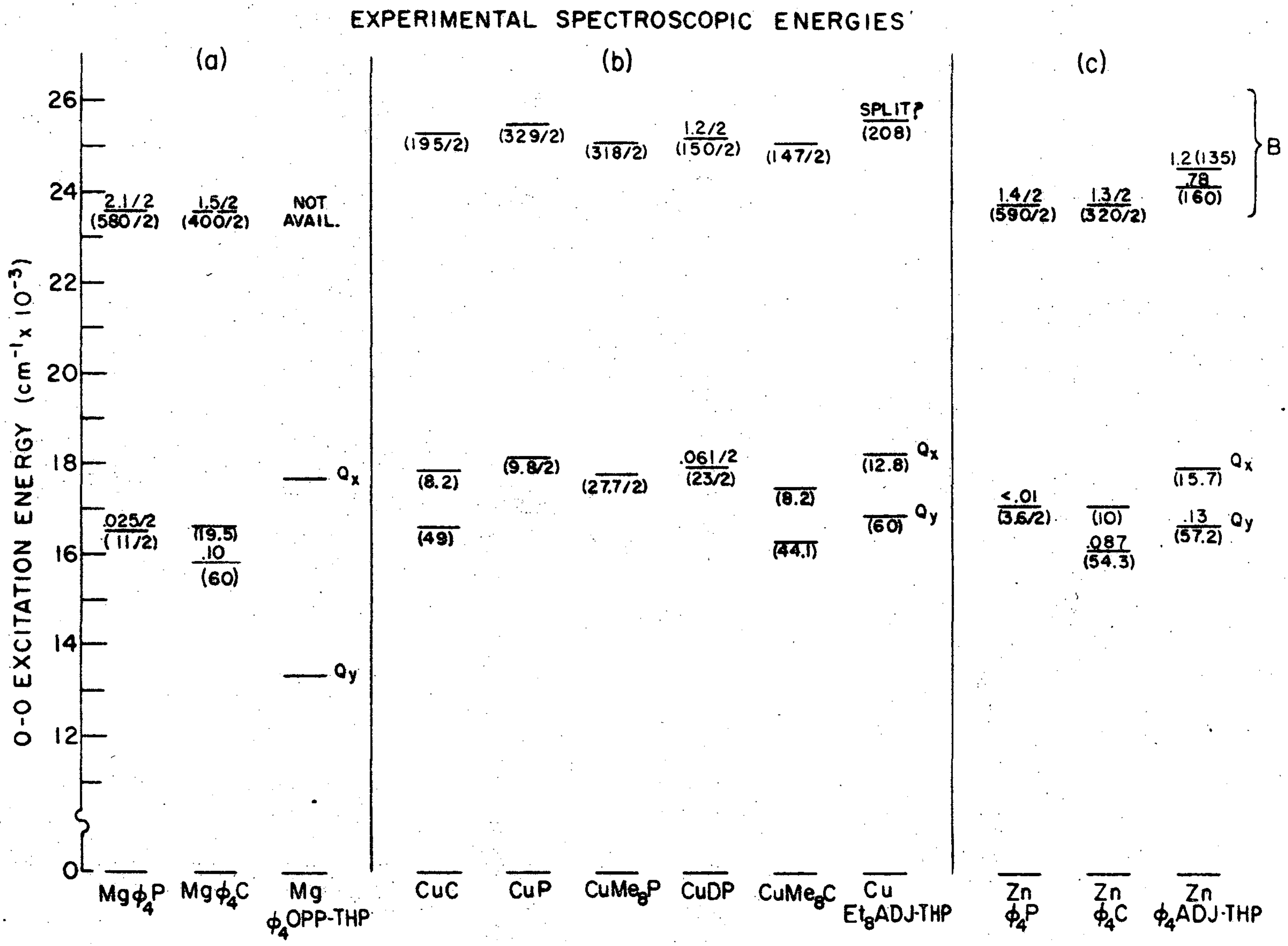

ENERGY
+.6
+.4
+.2
0
-.2
-.4
-.6
C1
C2
X
X
Y
Y
b1
b2
PORPHIN
C1
C2
X
X
Y
Y
b1
b2
CHLORIN
C1
C2
X
X
Y
Y
b1
b2
OPPTHP
C'
C''
b1
b2
ADJTHP

[illegible] Fig VA

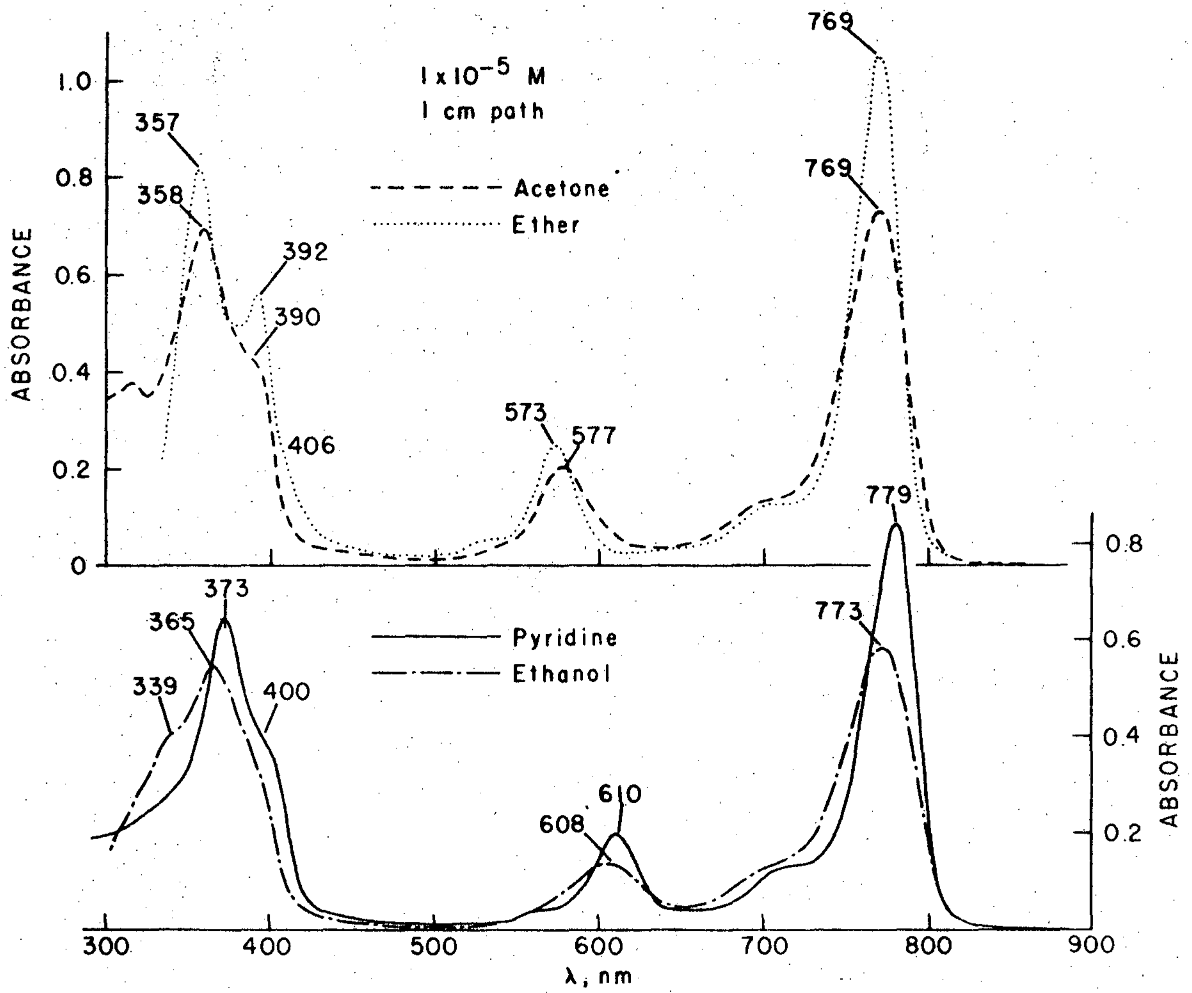


e_gy
e_gx
y
x
x
y
3a_2u
1a_1u
2a_2u
2b_2u
PORPHIN
e_gy
e_gx
y
x
x
y
a_2u
a_1u
x
a
CHLORIN
-2
-3
-4
-5
-8
-9
-10
-11
e_gy
e_gx
x
x
y
a_2u
a_1u
x
a
OPPTHP
e_gx
e_gy
x
y
y
x
a_2u
a_1u
y
a
ADJTHP


PORPHIN
PURE CONFIG
6-ORB MODEL
CI to 150 mμ
CHLORIN
PURE CONFIG
4-ORB MODEL
CI to 150 mμ
OPP-THP
PURE CONFIG
7-ORB MODEL
CI to 150 mμ
cm⁻¹ x 10⁻³
40
30
20
10
0
a2ueg
b2ueg
L
N
0.12
0.16
a1ueg
a2ueg
B
1.14
Q
.002
aegy
aegx
.036
.063
.085
.013
Ny
a2uegy
a1uegy
a2uegx
a1uegx
Bx
By
0.58
0.53
Qx
Qy
.001
.028
(η)
By
.67
Bx
.46
aegy
a2uegy
a1uegy
Nx
.11
a2uegx
a1uegx
Qx
.009
Qy
.052
y
x
N
N
N
N

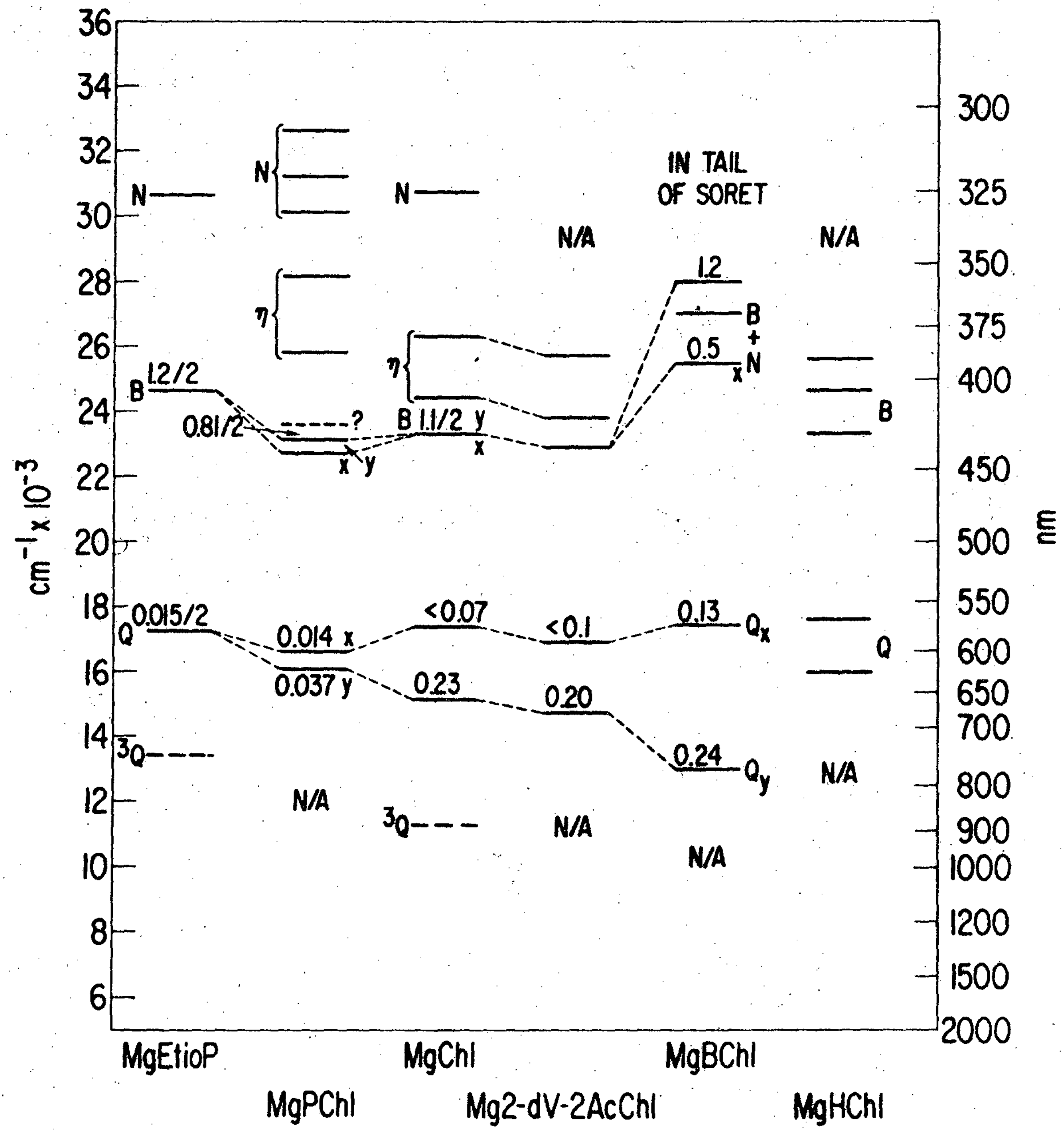

EXPERIMENTAL SPECTROSCOPIC ENERGIES
(a)
(b)
(c)
0-0 EXCITATION ENERGY (cm^{-1} x 10^{-3})
26
24
22
20
18
16
14
12
0
2.1/2
(580/2)
.025/2
(11/2)
1.5/2
(400/2)
(19.5)
.10
(60)
NOT AVAIL.
Qx
Qy
(195/2)
(8.2)
(49)
(329/2)
(9.8/2)
(318/2)
(27.7/2)
1.2/2
(150/2)
.061/2
(23/2)
(147/2)
(8.2)
(44.1)
SPLIT?
(208)
(12.8)
(60)
Qx
Qy
1.4/2
(590/2)
<.01
(3.6/2)
1.3/2
(320/2)
(10)
.087
(54.3)
1.2 (135)
.78
(160)
(15.7)
.13
(57.2)
Qx
Qy
B
MgΦ4P
MgΦ4C
Mg Φ4OPP-THP
CuC
CuP
CuMe8P
CuDP
CuMe8C
Cu Et8ADJ-THP
Zn Φ4P
Zn Φ4C
Zn Φ4ADJ-THP

BACTERIOCHLOROPHYLL ABSORPTION IN DIFFERENT SOLVENTS



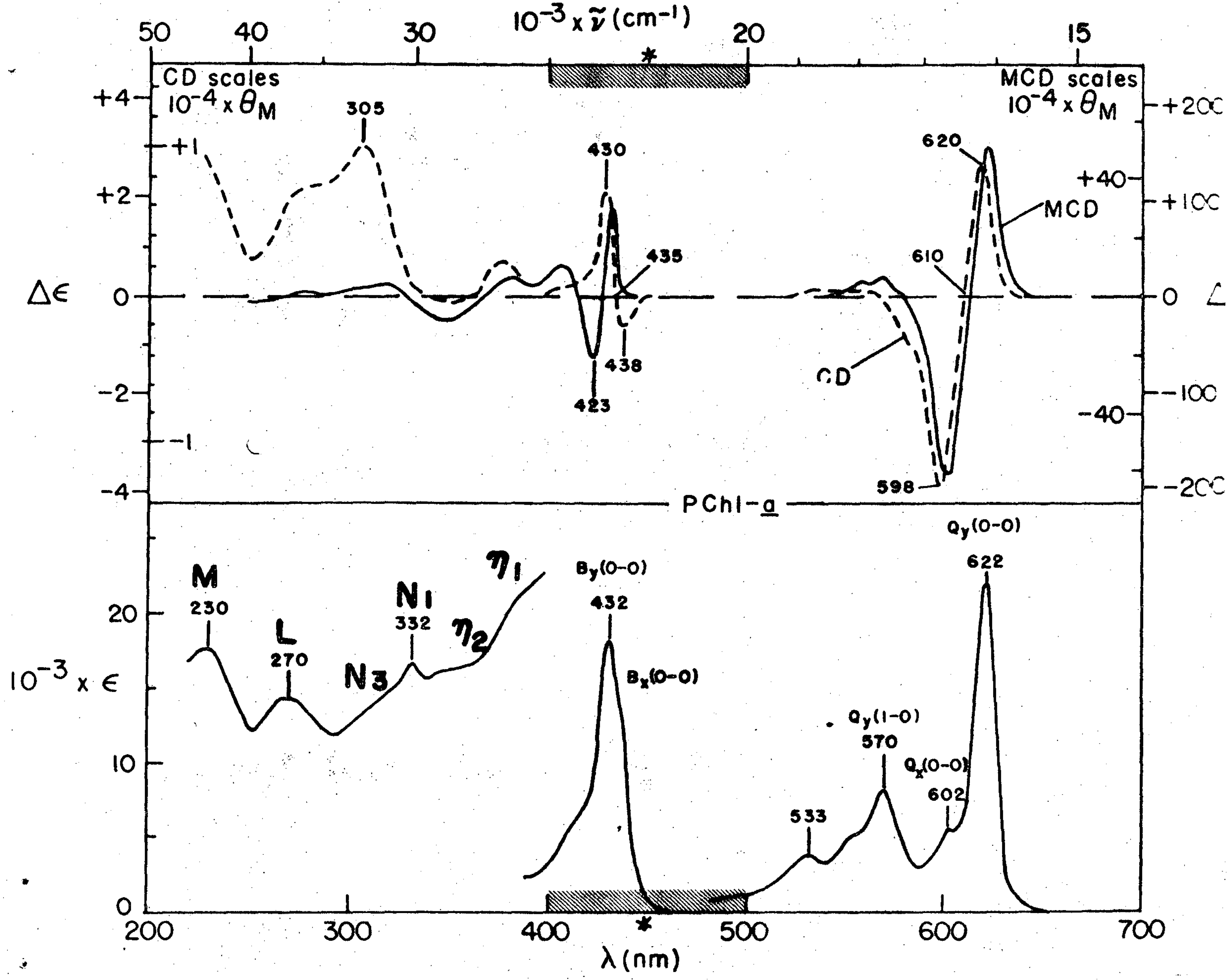
XBL 6911-5365

[illegible] Fig 7

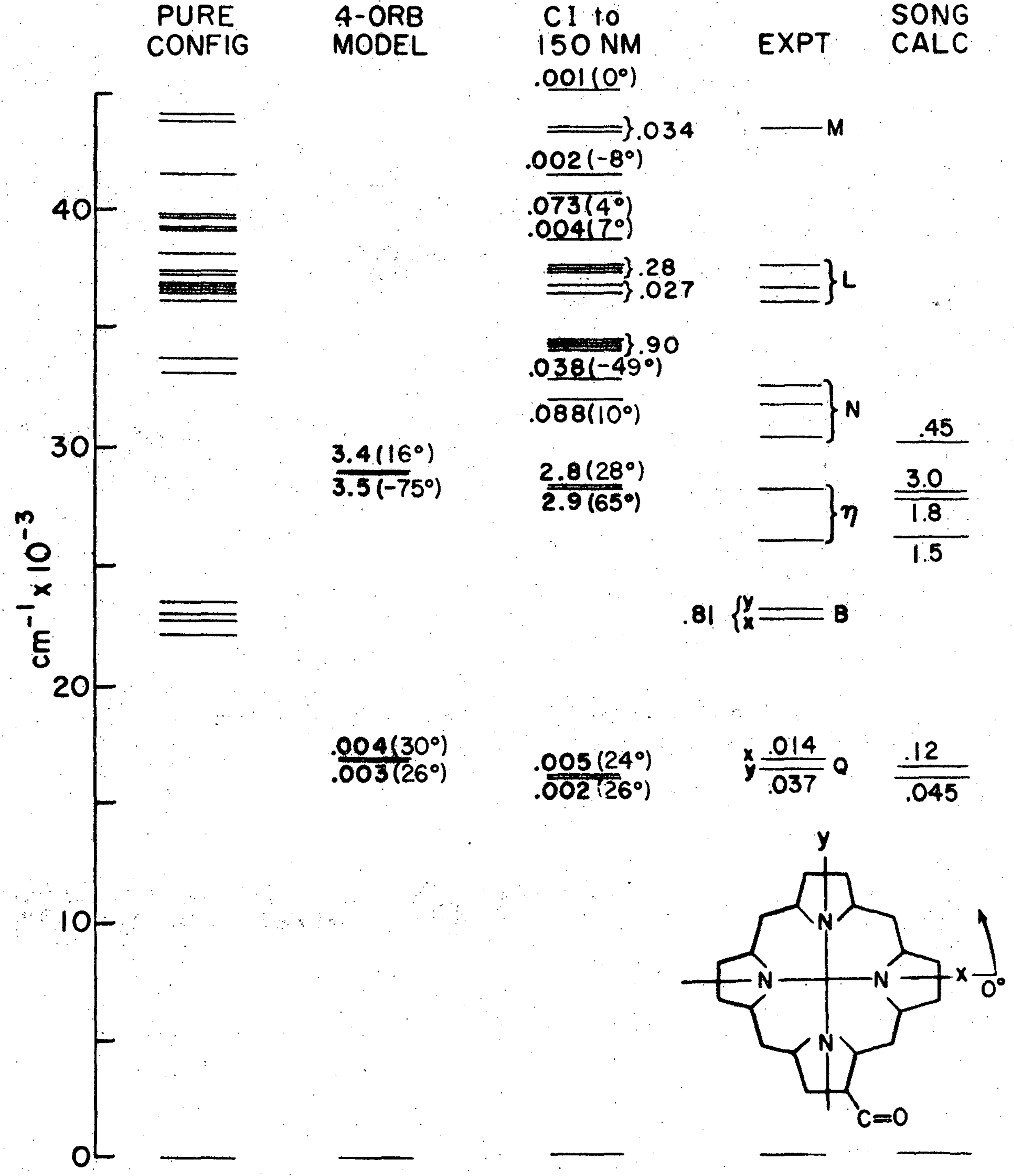


J. Mol Spectr. Weiss
Fig 8

Optical activity of PChl-$\underline{a}$ in ether

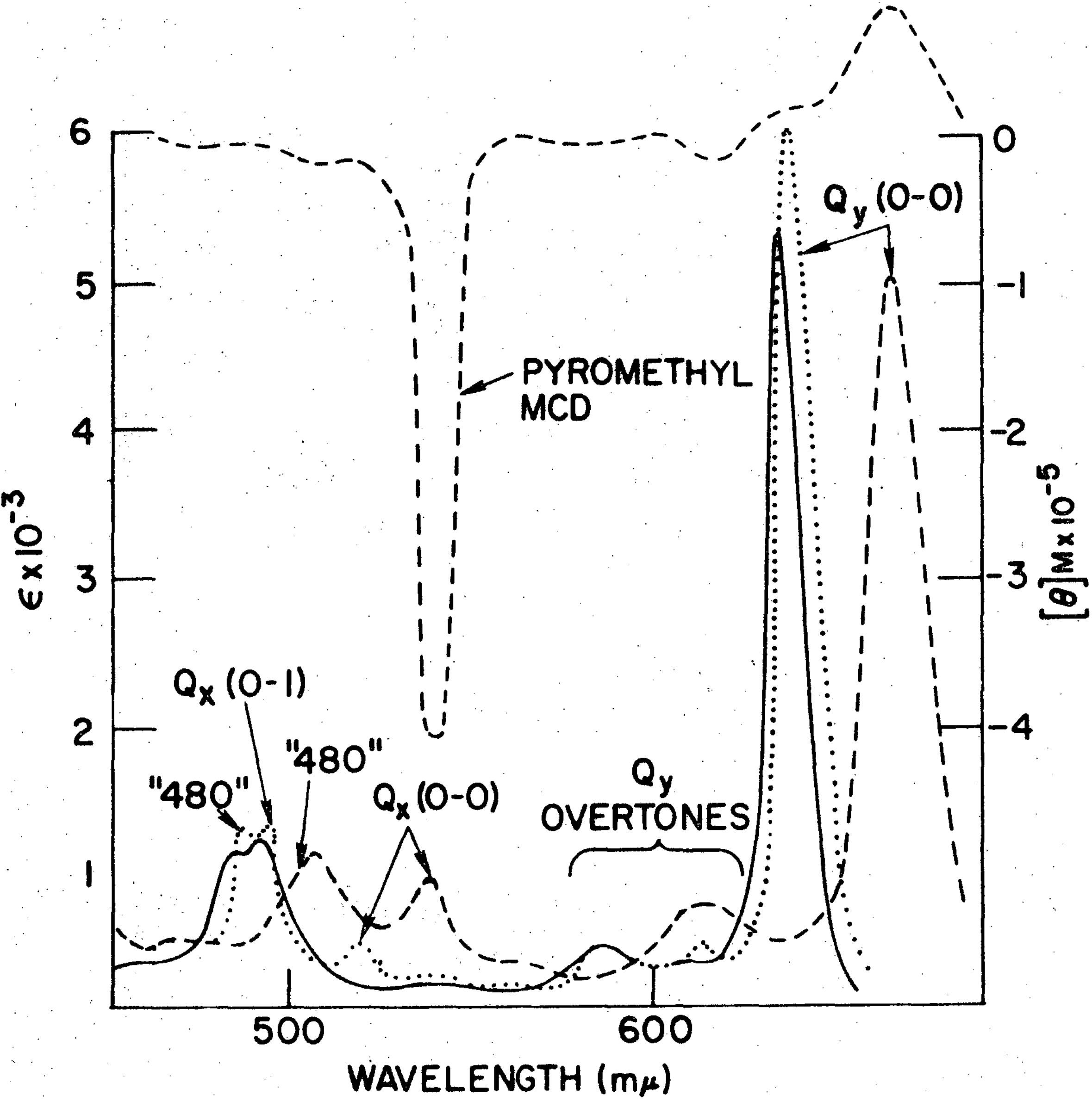


J Mol Spectr Weiss Fig 9

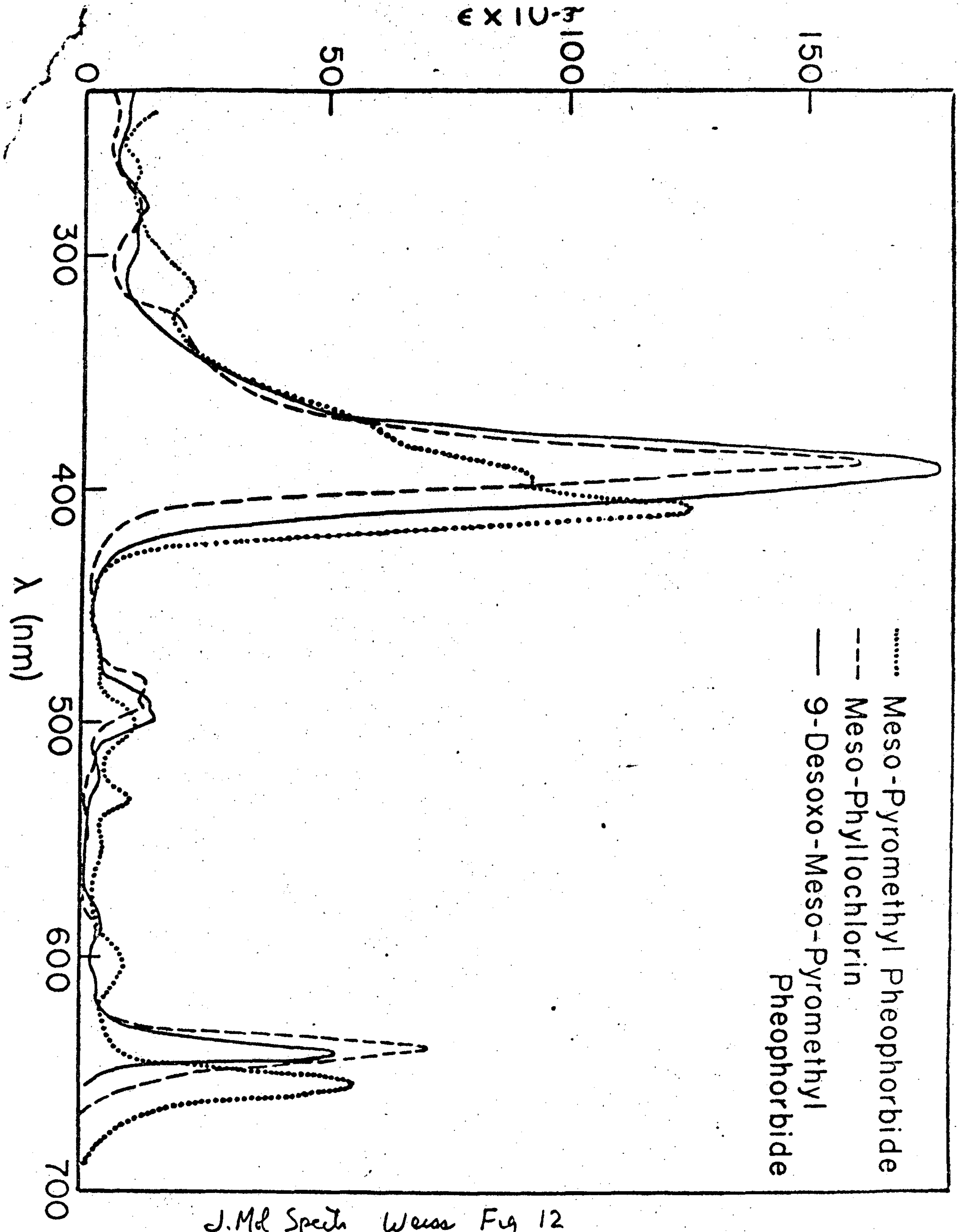


MONOCARBONYL PORPHIN (β_{CO}= -3.19 ev)

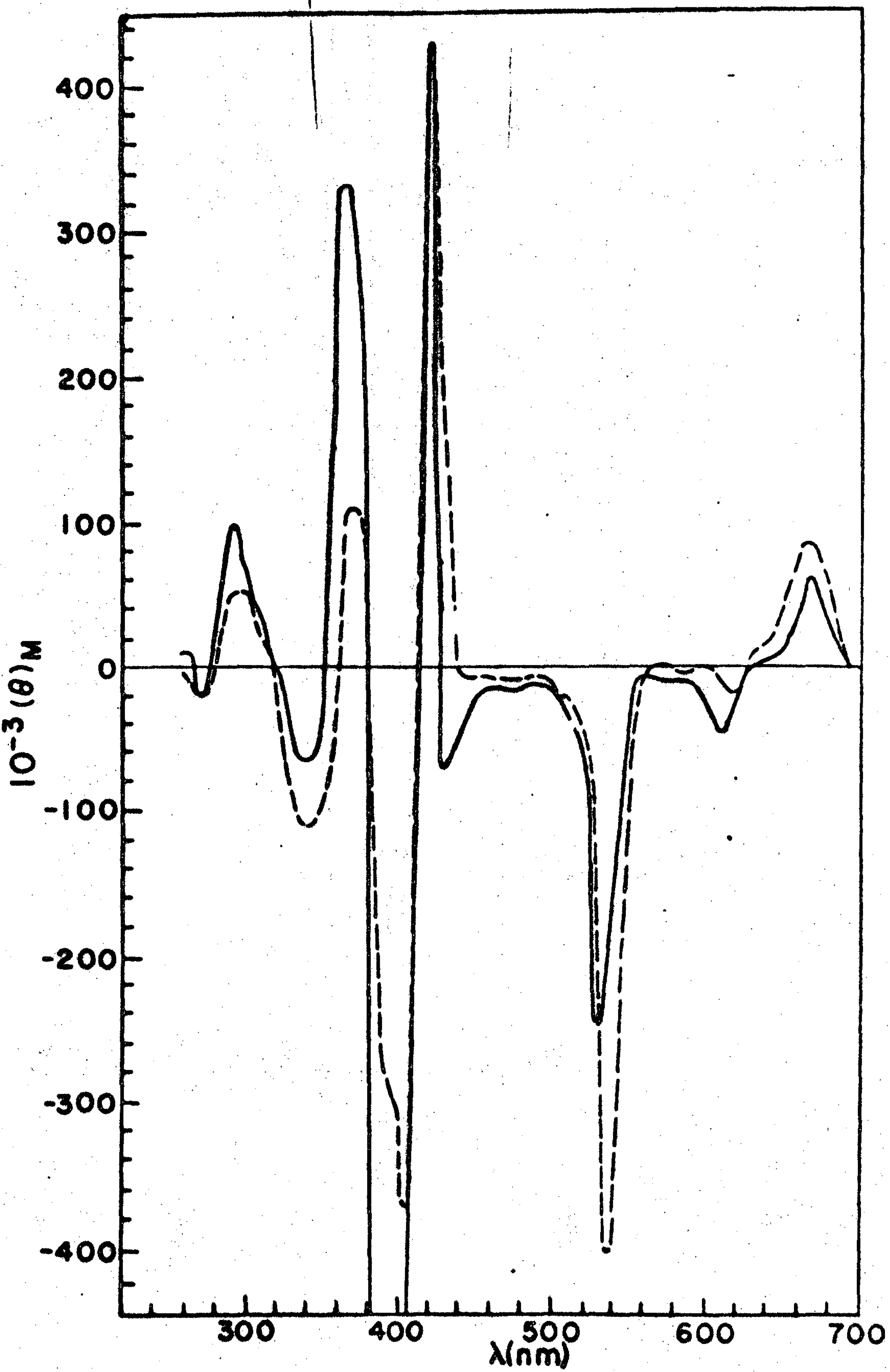
J. Mol Spectr Weiss Fig 10



J. Mol Spectr. Weiss Fig 11

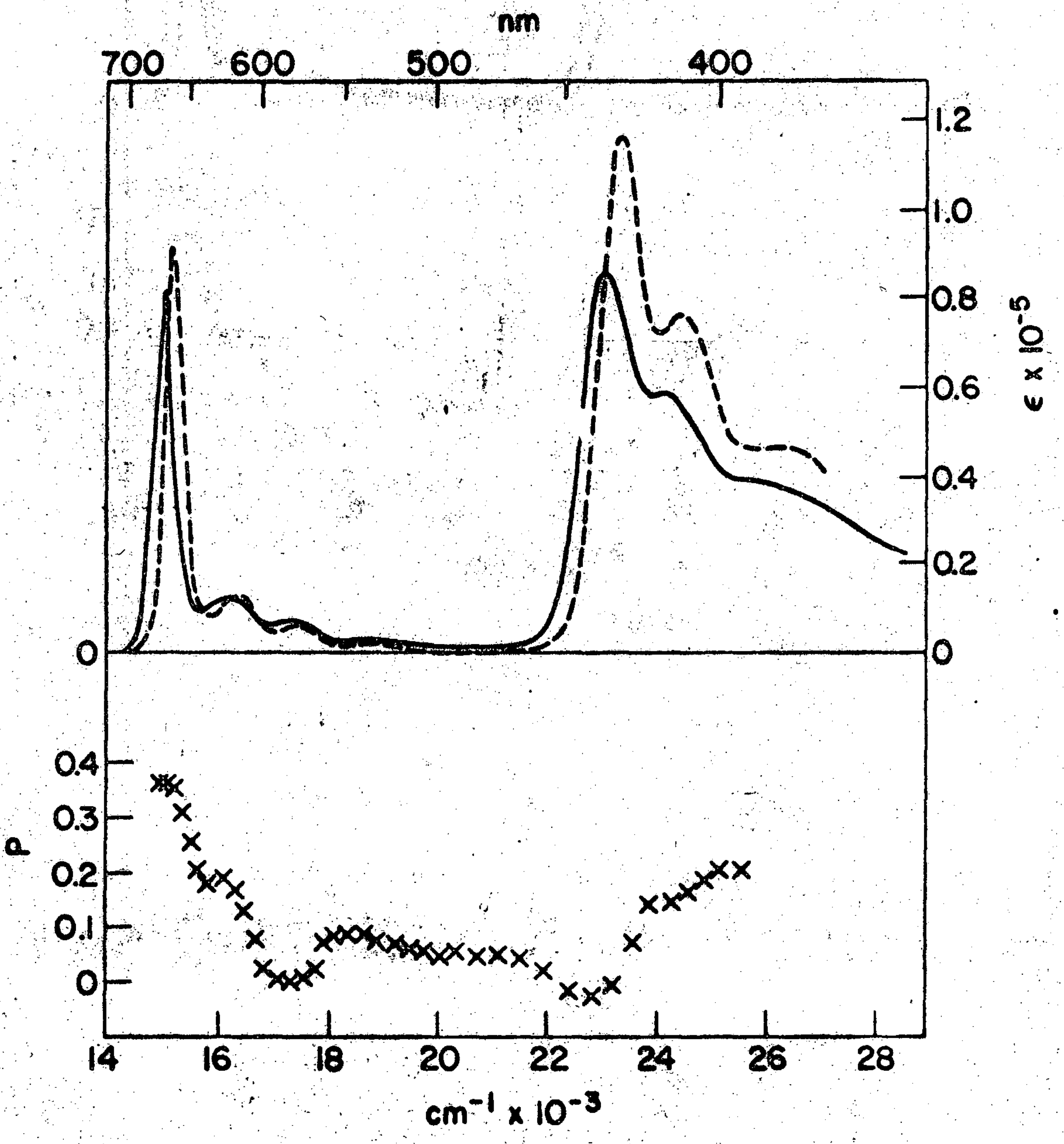


J.Mol Spectr Weiss Fig 12



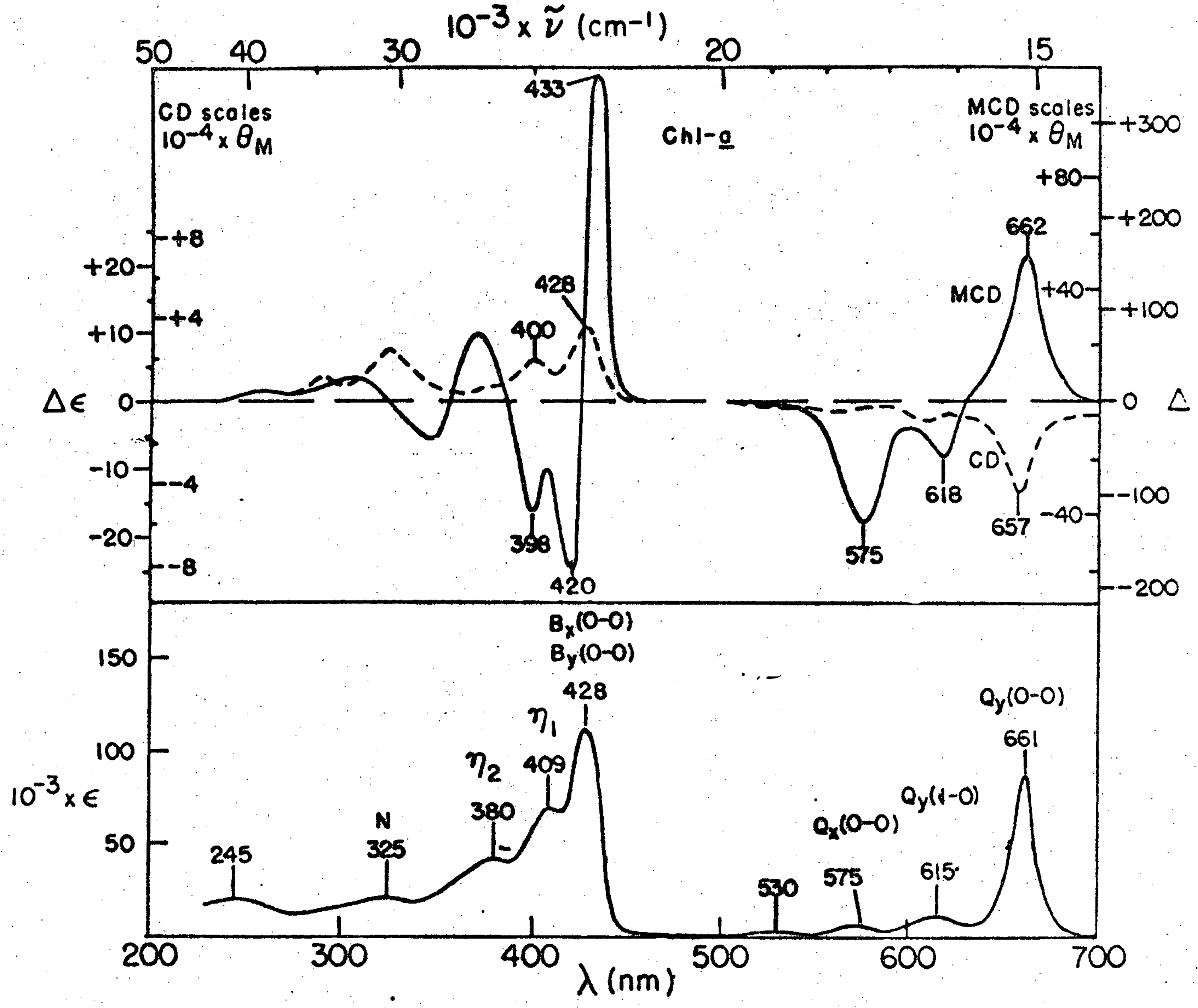
U
(1195)

J Mol Spectr   Weiss Fig 13



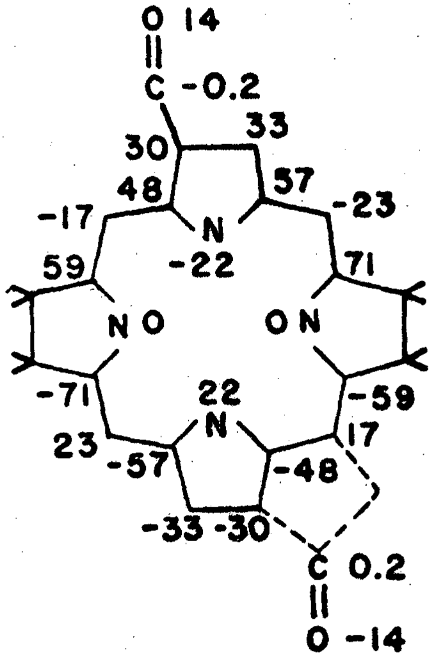
1 ML Spectra Weiss Fig 14

Optical activity of Chl-a in ether



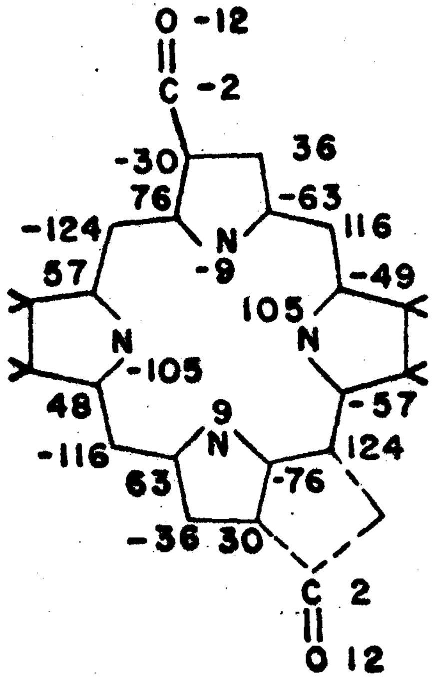
J Mol Spectr. Weiss Fig 15

NORMALIZED BACTERIOCHLOROPHYLL TRANSITION MONOPOLES



Qy

$\vec{q} = (6.24, 0.16)\, e \cdot \text{Å}$



Qx

$\vec{q} = (3.95, -0.49)\, e \cdot \text{Å}$

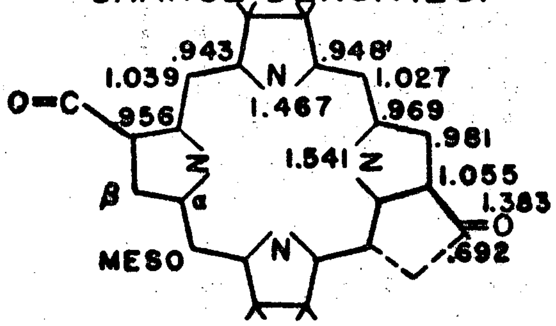
Ml Crects Weiss Fig 16

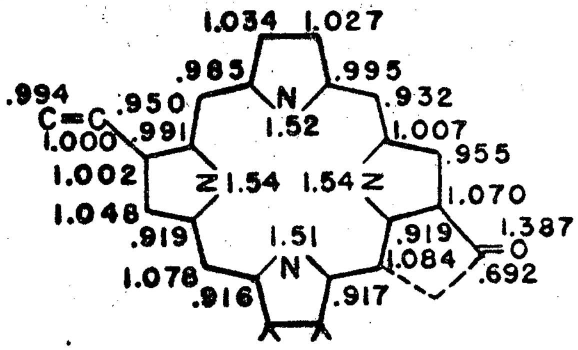
$\beta_{CO} = -2.36$

2,6 DICARBONYL OPP-THP
(BACTERIOCHLOROPHYLL)

2-VINYL-6-CARBONYL CHLORIN
(CHLOROPHYLL A)

CHARGE DENSITIES:





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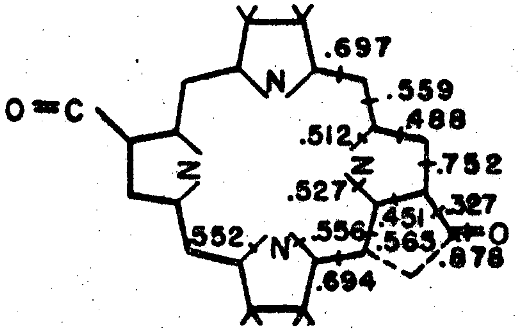
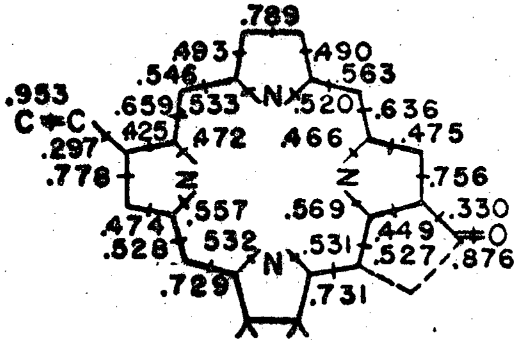


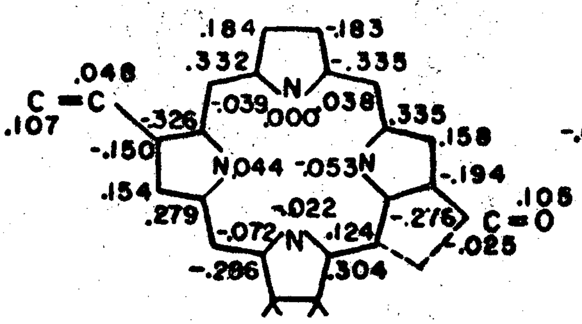


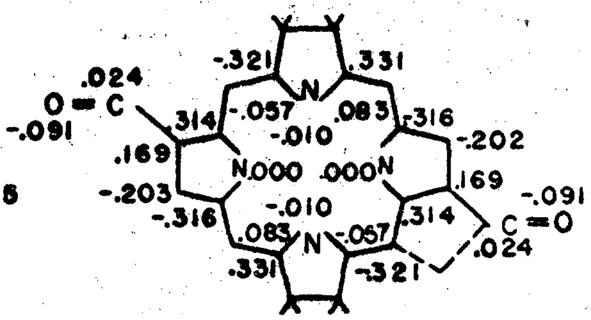
1 Ml Spectra Weiss Fig 17

$\beta = -2.36$

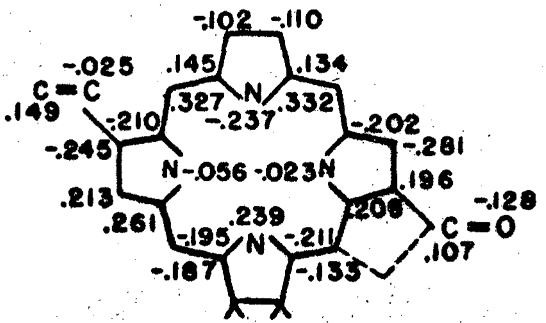
2-VINYL-6-CARBONYL CHLORIN

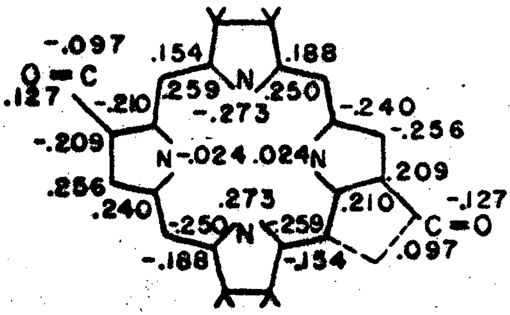
2,6-DICARBONYL OPP-THP





HIGHEST FILLED



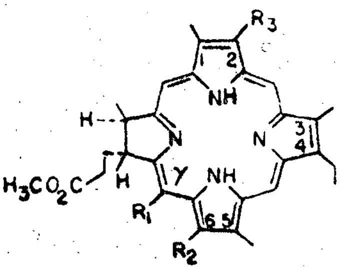


LOWEST UNFILLED

J. Mol Spectr Weiss Fig 18

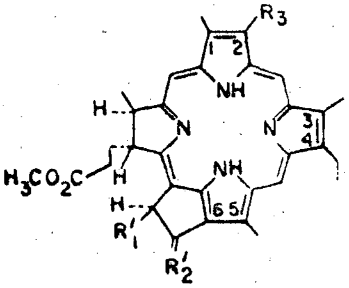
Table 1. Structure of Chlorins

(a)



No.	R_1	R_2	R_3	Compound
1	$CH_2CO_2CH_3$	CO_2CH_3	$CH{=}CH_2$	Chlorin e_6 trimethyl ester
2	H	CO_2CH_3	$CH{=}CH_2$	Rhodochlorin dimethyl ester
3	H	CO_2CH_3	CH_2CH_3	Meso-rhodochlorin dimethyl ester
4	H	H	CH_2CH_3	Meso-pyrrochlorin methyl ester
5	H	H	$CH{=}CH_2$	Pyrrochlorin methyl ester
6	CH_3	H	$CH{=}CH_2$	Phyllochlorin methyl ester
7	CH_3	H	CH_2CH_3	Meso-phyllochlorin methyl ester
8	H	CH_2CH_3	CH_2CH_3	Etiochlorin free base
9	$COCO_2CH_3$	CO_2CH_3	$CH{=}CH_2$	Purpurin 7 trimethyl ester

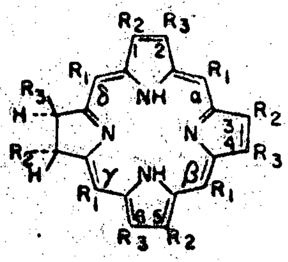
(b)



	R'_1	R'_2	R_3	
10	CO_2CH_3	O	$CH{=}CH_2$	Methyl pheophorbide a
11	H	O	$CH{=}CH_2$	Pyromethyl pheophorbide a
12	H	O	CH_2CH_3	Meso-pyromethyl pheophorbide a
13	H	H_2	CH_2CH_3	9-desoxo-meso-pyromethyl pheophorbide a

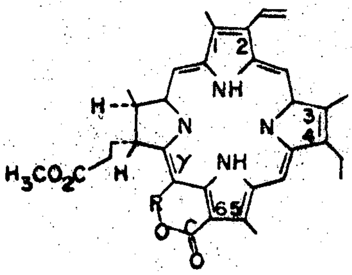
Table I. Continued

(c)



No.	R_1	R_2	R_3	Compound
14	H	CH_3	CH_2CH_3	Etiochlorin free base
15	H	H	H	Chlorin free base
16	C_6H_5	H	H	Tetraphenyl chlorin free base

(d)



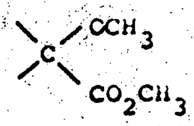
	R	
17	$\rangle C{=}O$	Purpurin 18-methyl ester
18	 $>C<^{OCH_3}_{CO_2CH_3}$	Purpurin 7-lactone methyl ether methyl diester

Table II * Spectra of Reduced Porphyrins - Comparison of Theory & Experiment

Compound	CI	β_{CO}(eV)	E_{Qy}(cm^{-1})	f^{d}_{Qy}	θ^{c}_{Qy}	ΔE_Q	E_{Qx}	f^{d}_{Qx}	θ^{c}_{Qx}	$E^{f}_{B_1}$	$f^{d}_{B_1}$	$\theta^{c}_{B_1}$	ΔE_B	$f^{d}_{B_2}$	$\theta^{c}_{B_2}$	
Chlorin: Theory	4-orb	-	17030	.195	90°	1410	18440	.030	0°	29100	2.55	90°	260	2.95	0°	
	CI to 150	-	16170	.14	90°	1540	17710	.027	0°	28580	2.32	0°	170	2.33	90°	
Expt^{o}	-	-	16390	(56)^{g}	b	1280	17670	(7.7)^{g}	b	24880	(309)^{g}	b	0?^{i}	-	-	
6-carbonyl chlorin: Theory	4-orb	-3.19	16900	.23	92°	1560	18460	.043	11°	29010	2.60	71°	190	2.81	-15°	
	CI to 150	-3.19	16010	.17	92°	1690	17700	.037	9°	28350	2.36	29°	210	2.32	61°	
	CI to 150	-2.36	15960	.18	92°	1740	17700	.042	12°	28100	2.45	47°	360	2.21	-47°	
Expt^{p}	-	-	15150	.13	b	2150	17300	(9.0)^{g}	b	23150^{a}	1.4^{h}	b	0^{j}	-	b	
2-Vinyl-6-Carbonyl Chlorin:Theory	4-orb	-3.19	16820	.26	91°	1580	18400	.051	24°	28660	2.59	85°	210	2.76	-4°	
	CI to 150	-3.19	15990	.21	90°	1770	17760	.046	24°	27440	1.78	-65°	690	2.34	17°	
	CI to 155	-2.36	15980	.22	91°	1780	17760	.052	27°	27330	1.92	-83°	610	2.16	23°	
Chlorophyll a: Theory	Song Calc.[28]	-3.00	15720	.33	∥	2490	18210	.08	⊥	24760	3.07	∥	1700	3.28	⊥	
													2500	3.38	∥	
Expt^{q}	-	-	15100	.23^{n}	∥	2200	17300	(9.5)^{g}	⊥	23260	1.1^{h}	m	0^{j}	-	m	
										$E^{u}_{B_x}$	f_{B_x}	$\theta^{c}_{B_x}$	E_{B_y}	f_{B_y}	$\theta^{c}_{B_y}$	E_{N_x}
OPP-THP:Theory	7-orb	-	15530	.59	90°	2160	17690	.124	0°	32310	1.49	0°	32810	2.90	90°	32300
	CI to 150	-	14930	.52	90°	2190	17120	.106	0°	32010	1.93	0°	32570	2.91	90°	30230
	Otten Calc.[29]	-	12430	.56	90°	3400	15830	.04	0°	29980	2.24	0°	31190	2.07	90°	26100
Expt^{r}	-	-	13330	b	b	4200	17530	b	b	b	b	b	b	b	b	b
2 6 Dicarbonyl OPP-THP:Theory	4-orb	-3.19	15220	.67	92°	2360	17580	.154	5°	31030	2.48	9°	32450	2.94	-82°	-
	CI to 150	-3.19	14590	.62	92°	2330	16920	.129	7°	31290	2.19	32°	31960	2.66	-73°	29720
	CI to 160	-2.36	14530	.67	92°	2390	16920	.140	7°	30790	2.41	41°	31580	1.96	-68°	29450
Mg Bacteriochlorophyll:Theory	Song Calc.[28]	-3.00	13620	.90	∥	4120	17740	0.11	⊥	28310	1.36	⊥	29920 30080	0.62 0.18	∥ ⊥	26800
Expt^{s}	-	-	12940	.24	∥	4390	17330	.13	⊥	25580	.5	⊥	27930	1.2^{k}	∥	25500

* All spectroscopic energies in wave numbers. x axis passes through the reduced double bond(s). Note that in Table IV of Ref. 6, the headings $\underline{Q}_x$ and $\underline{Q}_y$ are reversed.

[a] Degenerate

[b] not available

[c] angle of polarization measured from +x axis

[d] oscillator strength

[e] unresolved

[f] B_1 and B_2 are the Soret daughters that are lower and higher in energy, respectively

[g] extinction coefficient

[h] includes Soret and η_1 band

[i] shape of spectrum not given but band assumed not split

[j] assuming that shoulder represents a separate transition (see text)

[k] relative intensities depend on solvent

[m] net polarization of overlapping $\underline{B}_x$ and $\underline{B}_y$ is ⊥

[n] Oscillator strength in ether[17] and in carbon tetrachloride[15]. Ref. 13 gives f = .16 for $\underline{Q}_y$, .03 for $\underline{Q}_x$, in ether

[o] Mg Chlorin in benzene[54]

[p] Mg Chlorobium Chlorophyll in ether[17]

[q] Mg Chlorophyll a in ether[17]

[r] Mg Tetraphenyl OPP-THP in benzene[53]

[s] Mg bacteriochlorophyll in ether[17]

Table III - Effects of Perturbations in Chlorin Spectra ∓

1 Ref.	2a Compounds Compared #1	2b #2	3 Pertubation	4	5a Q_y ΔE	5b ϵ_1/ϵ_2	6 Q_x ϵ_1/ϵ_2	7a B ΔE	7b ϵ_1/ϵ_2
54,89	(15)	(4)	$H_7 \rightarrow \underline{\mathrm{alk}}_7{}^{d}$	Expt	-185	0.81	0	-190	.99
89,71	(4)	(8)^e	H → $\underline{\mathrm{alk}}$	Expt	+80	1.05	.80	+60	.87
71,90	(8)^e	(3)	6-$\underline{\mathrm{alk}}$→6-CO^a	Expt	-255	.94	1.32	*	*
72	(13)	(12)	6-$\underline{\mathrm{alk}}$→6-CO^b	Expt	-400	.90	0.35	-1010	1.30
			$H_2 \rightarrow CO$	Theory	-170^f	.81^c	.68^c	-270	1.00^c
90,9	(3)	(2)	2-$\underline{\mathrm{alk}}$→2-V	Expt	-300	1.06	.64	*	*
89,90	(4)	(5)	2-$\underline{\mathrm{alk}}$→2-V	Expt	-300	1.37	1.45	*	*
9	(12)	(11)	2-$\underline{\mathrm{alk}}$→2-V	Expt	-300	1.06	1.03	-300	1.08
71,90	(7)	(6)	2-$\underline{\mathrm{alk}}$→2-V	Expt	-350	1.03	0.74	*	*
			$H_2 \rightarrow V_2$	Theory	+20	.84^c	.82^c	-430^c	1.10^c
9	(2)	(1)	γ-H → γ-Me	Expt	+20	1.15	.94	-60	.97
89,71	(4)	(7)	γ-H → γ-Me	Expt	+50	1.22	1.38	+130	1.13
90	(5)	(6)	γ-H → γ-Me	Expt	-130	.92	.61	*	*
9	(1)	(10)	close pentenone isocyclic ring	Expt	-50	.96	.49	-550	1.29
71	(7)	(13)	Close pentene isocyclic ring	Expt	+120	.96	.67	-130	.92

∓ Explanation: This table compares the spectra of pairs of closely related compounds in column 2. These are chosen to exemplify the substituent perturbations listed in column 3. (Here $\underline{\mathrm{alk}}$ refers to any α-saturated substituent, 6-CO to any α-carbonyl substituent in the 6-position, V to vinyl.) ϵ_1/ϵ_2 is the ratio of the extinction coefficients of the two compounds. Theoretical predictions are based on SCMO-CI calculations on chlorin with only the indicated substitution (average of available calculations). $f_B = f_{B_x} + f_{B_y}$. ϵ_B is the experimental Soret maximum whether or not the band is split. For numbering of atoms see Table I. All spectra in dioxane except as noted by ^{d}.

Notes:
- * spectrum not available
- a no isocyclic ring
- b with isocyclic ring
- c ratio of oscillator strengths
- d benzene solvent
- e Soret band is octamethyl chlorin free base^{55}
- f Shoud be compared with $-360 = -185 + 80 - 255$

TABLE IV. Predicted Energy of Lowest Triplet Configurations

Compound	β_{co} (eV)	${}^3E_1$	${}^3E_2$	${}^3E_3$	${}^3E_4$ (cm^{-1})
Porphin	---	11160	11160	14540	14540
Carbonyl Porphin	-2.36	10870	11370	14230	14770
	-3.19	10910	11330	14290	14710
Protochlorophyll	(Song)	12740		15080	
Chlorin		11070	11440	15850	16970
6-Carbonyl Chlorin	-2.36	11040	11500	16150	17240
	-3.19	11040	11470	16090	17190
Chlorophyll *a*	(Song)	11050		15729	
ADJ-THP		11210	14390	16780	17050
OPP-THP		5630	9810	17030	22050
2,6-Carbonyl OPP-THP	-2.36	5520	9540	17290	22190
	-3.19	5540	9570	17210	22120
Bacteriochlorophyll *a*	(Song)	7100		14040	

TABLE V IONIZATION POTENTIALS AND ELECTRON AFFINITIES
(Predicted by Koopman's Theorem)

Porphyrins	β_{CO} (eV)	I.P. (eV)	E.A. (eV)
Porphin	—	8.45	3.81
Carbonyl Porphin	-2.36	8.59	4.06
	-3.19	8.57	4.00
Vinyl Porphin		8.44	3.81
4,6-Dicarbonyl Porphin	-2.36	8.73	4.18
	-3.19	8.68	4.11
2,6-Dicarbonyl Porphin	-2.36	8.73	4.28
4,6-Divinyl Porphin	—	8.43	3.84
Protochlorophyll *a*	-2.36	8.58	4.08
	-3.19	8.56	4.02
Chlorins			
Chlorin	—	8.48	3.94
6-Carbonyl Chlorin	-2.36	8.64	4.15
	-3.19	8.61	4.10
4,6-Dicarbonyl Chlorin	-2.36	8.78	4.29
	-3.19	8.73	4.22
Chlorophyll	-2.36	8.62	4.16
	-3.19	8.59	4.12
Tetrahydroporphins			
ADJ-THP	—	8.22	3.48
OPP-THP	—	8.11	4.16
2,6-Dicarbonyl OPP-THP	-2.36	8.43	4.58
	-3.19	8.37	4.50

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