Magnetic Circular Dichroism Studies. Part XXX.[1] Vibronic Intensity in Metalloporphyrins

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We have studied the vibronic structure in the $Q(1,0)$ band of several metalloporphyrins, using explicit relations based on the four orbital model for porphyrins, and find that most of the absorption intensity is due to vibronic coupling of the quasi-forbidden Q or $E_u{}^1$ state with the strong B or $E_u{}^2$ state (Soret band). We also attribute significant intensity to Franck–Condon progressions. The Franck–Condon contribution is manifested primarily in the m.c.d. A value of the $Q(0,0)$ band because the other vibronic components consist of positive and negative A terms, and tend to cancel. The theoretical treatment shows that the variation (with configuartion interaction) of the intensity due to active vibrations is uniquely determined by the symmetry of the vibration. This behaviour has been used to assign tentatively the symmetries of the vibrations responsible for bands in the Q or $E_u{}^1$ excited state. A comparison of our assignment with that previously obtained by Spiro and Strekas using resonance Raman spectroscopy leads to a general confirmation of their results. In addition, we have been able to define further the accidental degeneracies observed in the Raman spectra and hence to refine the assignment.

THE first definitive theoretical study of the m.c.d. of porphyrins was one by Stephens *et al.*[2] in which they applied the free electron model [3] and Gouterman's four orbital model [4] to the calculation of the magnetic moment of the 0–0 band of the lowest porphyrin excited state ($E_u{}^1$ state or Q band). Other work, both experimental and theoretical, has centred around the measurement of the magnetic moment of the $Q(0,0)$ band and the problems encountered when the degeneracy (D_{4h}) of the $Q(0,0)$ band is lowered by zero-field splitting.[5-7] The vibronic structure in the $Q(1,0)$ region has been mentioned [5,7-9] and Gouterman and his co-workers [10,11] have shown that vibronic borrowing can lead to an inversion of the normally positive A terms.[12] These negative A terms are due to a symmetry reversal of the phase of the electric moments when the vibration responsible for the borrowed intensity is b_{1g} or b_{2g} in symmetry (D_{4h}) † and have been observed by Gale *et al.*[8] We also have observed negative A terms, in the m.c.d. spectrum of octaethylporphyrin dication,[13] and have inferred their existence in zinc and palladium porphine.[14] Further, Spiro and Strekas [15] have observed depolarized (b_{1g} or b_{2g}) bands in the resonance Raman spectra of heme porphyrins.

In a series of papers [10,11,16] Gouterman and his co-workers have applied the cyclic polyene model to the calculation of vibronic intensities in porphyrins. This model has two shortcomings that will be difficult to surmount. First, the cyclic polyene model gives zero intensity in the $Q(0,0)$ band, whereas real porphyrins deviate considerably from this situation. Secondly, a limited number of vibrational modes are considered. As we shall see several more modes are experimentally observed than are theoretically considered. Even so, the cyclic polyene model has had considerable success in predicting vibronically induced m.c.d. The dominance of the A terms was predicted and is observed. Also, negative A terms occur naturally in the theory.

However, for the reasons stated, we felt that a more flexible model was needed. In this communication, we report the results of applying the four orbital model to the vibronic problem in porphyrins. (A recent CNDO calculation by Maggiora on certain porphins [17] indicates that the four orbital model is quite reasonable in these cases.) To do this, we use the Herzberg-Teller [18-22] formalism and apply the theory in its simplest form. This entails the basic assumption that the vibrational integrals are constant for a given porphyrin skeleton. We then obtain a functional dependence on Gouterman's configuration interaction parameter α for the intensity

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† D. J. Robbins (*Theor. Chim. Acta*, 1974, **33**, 51), in a paper published after we had submitted this manuscript, has shown that Jahn–Teller effects may reverse the sign of A terms in E states of molecules with C_{4v} symmetry. Since the Jahn–Teller active modes for an E_u state in D_{4h} symmetry are the b_{1g} and b_{2g} modes, it is possible that these effects are responsible for the inversion of the A terms.

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[9] R. A. Shatwell and A. J. McCaffery, *J.C.S. Chem. Comm.*, 1973, 546.

[10] M. H. Perrin, M. Gouterman, and C. L. Perrin, *J. Chem. Phys.*, 1969, **50**, 4137.

[11] A. J. McHugh, M. Gouterman, and C. Weiss, *Theor. Chim. Acta*, 1972, **24**, 346.

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[13] G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *Ann. New York Acad. Sci.*, 1973, **206**, 223. Note that the sign convention for A values is reversed in refs. 10, 11, and 13 from that in ref. 12. In this communication, we have chosen our signs to agree with ref. 12. Thus a normal A term is positive here.

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[15] T. G. Spiro and T. C. Strekas, *J. Amer. Chem. Soc.*, 1974, **96**, 338.

[16] M. H. Perrin, *J. Chem. Phys.*, 1973, **59**, 2090.

[17] G. M. Maggiora, *J. Amer. Chem. Soc.*, 1973, **95**, 6555.

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[19] A. C. Albrecht, *J. Chem. Phys.*, 1960, **33**, 156.

[20] A. C. Albrecht, *J. Chem. Phys.*, 1960, **33**, 169.

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[22] A. D. Liehr, *Z. Naturforsch.*, 1958, **13a**, 311, 596.

of the vibronic bands, and find that it is possible to assign the symmetries of the vibrations responsible for these bands by studying the variation of intensity with configuration interaction. Our assignments are compared with those of Spiro and Strekas,[15] and a composite assignment is made.

THEORY

We assume, with Herzberg and Teller,[18] that the Hamiltonian may be written as (1) where $H_r' \equiv \partial H_{e\text{-}n}/\partial\xi_r$, H_0

$$H = H_0 + \Sigma H_r'\xi_r \qquad (1)$$

is the Hamiltonian at the equilibrium position, and ξ_r is the rth normal mode. We consider only adiabatic coupling, ignoring Jahn–Teller effects, and are led to a set of Born–Oppenheimer excited states such as (2) * where $|Q_x\rangle^0$ and

$$|Q_x\rangle|q\rangle = |Q_x\rangle^0|q\rangle + \sum_{K,k,r} \frac{\langle K|H_r'|Q_x\rangle^0}{\Delta E} \langle k|\xi_r|q\rangle|K\rangle^0|k\rangle \qquad (2)$$

$|K\rangle^0$ are the $E_{ux}{}^1$ and other excited electronic states at the equilibrium nuclear geometry, $|q\rangle$ and $|k\rangle$ are the associated vibrational states, and ΔE is the energy separation of the states $|Q_x\rangle^0|q\rangle$ and $|K\rangle^0|k\rangle$. One experimental quantity of interest is the dipole strength of a given vibronic band. The intensity of the 0—1 band based on the qth vibrational mode is given by equation (3). Insertion

$$D(q) = 2|\langle 0|\langle A_{1g}|\boldsymbol{m}|Q_x\rangle|q\rangle|^2 \qquad (3)$$

of equation (2) into (3) yields (4).† We may simplify

$$D(q) = 2|\langle A_{1g}|\boldsymbol{m}|Q_x\rangle^0|^2|\langle 0|q\rangle|^2 + 2|\sum_{K,k,r} \frac{\langle K|H_r'|Q_x\rangle^0}{\Delta E}\langle k|\xi_r|q\rangle|^2 |\langle A_{1g}|\boldsymbol{m}|K\rangle^0|^2|\langle 0|k|\rangle^2 \qquad (4)$$

equation (4) by noting that the second excited π–π^* state ($E_u{}^2$ state or B band) is responsible for most of the vibronic intensity in the Q band.[10] K is henceforth restricted to the B_x and B_y states, and vibronic mixing of the ground and this excited state is ignored.

At this point, we may extract two experimental quantities, the dipole strength of the $Q(0,0)$ and $B(0,0)$ bands, obtaining equation (5).

$$D(q) = D_{Q(0,0)}|\langle 0|q\rangle|^2 + D_{B(0,0)}|\sum_{K,k,r} \frac{\langle K|H_r'|Q_x\rangle^0}{\Delta E} \langle k|\xi_r|q\rangle\langle 0|k\rangle|^2 \qquad (5)$$

Since we have assumed that all vibrational integrals are constant for a given porphyrin skeleton and since ΔE is approximately constant, the remaining factor is $\langle K|H_r'|Q_x\rangle^0$. We may expand this factor by using the states of the reference porphyrin of Gouterman's four orbital model. These states apply to a porphyrin in which the a_{1u} and a_{2u} orbitals are accidentally degenerate, leading to complete mixing of the lowest two one-electron excitations. The states of other porphyrins at the equilibrium geometry are given in terms of the states of the reference porphyrin by equation (6) where α is Gouterman's con-

$$\begin{aligned} |Q_x\rangle^0 &= \sin\alpha|B_x{}^0\rangle + \cos\alpha|Q_x{}^0\rangle \qquad (6)\\ |Q_y\rangle^0 &= -\sin\alpha|B_y{}^0\rangle + \cos\alpha|Q_y{}^0\rangle\\ |B_x\rangle^0 &= \cos\alpha|B_x{}^0\rangle - \sin\alpha|Q_x{}^0\rangle\\ |B_y\rangle^0 &= \cos\alpha|B_y{}^0\rangle + \sin\alpha|Q_y{}^0\rangle \end{aligned}$$

figuration interaction parameter ($\alpha = 0$ for a polyene) and the superscript zero inside the ket indicates the appropriate polyene state.

Since H_r' is a one electron operator, we may evaluate $\langle K|H_r'|Q_x\rangle^0$ in terms of orbital matrix elements. The results are in the form of equation (7a) where the relationships (7b) apply. The symmetry labels in equation (7b)

$$\begin{aligned} \langle B_x|H_r'|Q_x\rangle^0 &= \cos 2\alpha(-b_{1g} - a_{1g}) \qquad (7a)\\ \langle B_y|H_r'|Q_x\rangle^0 &= b_{2g} + \cos 2\alpha a_{2g} \end{aligned}$$

$$\begin{aligned} a_{1g} &= -(a_{2u}|H_r'|a_{2u}) + (a_{1u}|H_r'|a_{1u}) \qquad (7b)\\ a_{2g} &= -(a_{2u}|H_r'|a_{1u})\\ b_{1g} &= (e_{gy}|H_r'|e_{gy}) - (e_{gx}|H_r'|e_{gx})\\ b_{2g} &= (e_{gy}|H_r'|e_{gx}) \end{aligned}$$

refer to the symmetry which H_r' must have in order to couple the indicated orbitals. Since $|q\rangle$ must have the same symmetry as ξ_r and H_r' in order to have a nonzero value for the vibronic term of equation (5) ($|k\rangle$ must be totally symmetric), these labels in fact are the symmetries of the vibrations responsible for the vibronic coupling. If we also assume that most of the intensity for a vibronic band is given when ξ_r is the normal mode associated with the excited state vibrational level, we obtain equation (8) where a_{1g} *etc.* are constants for each

$$D(q) = D_{Q(0,0)}|\langle 0|q\rangle|^2 + D_{B(0.0)}|[\cos 2\alpha(-b_{1g} - a_{1g} + a_{2g}) + b_{2g}]/\Delta E|^2 \qquad (8)$$

vibronic band, only one of which is nonzero for any particular vibronic band. Finally, we note that $D_{Q(0,0)}$ is related to $D_{B(0.0)}$ in the four orbital model and obtain equation (9) where $a_{1g}{}^{FC}$ is the Franck–Condon overlap

$$D(q)/D_{B(0.0)} = \sin^2\alpha(a_{1g}{}^{FC})^2 + [a_{1g}{}^2 + a_{2g}{}^2 + b_{1g}{}^2]\cos^2 2\alpha + b_{2g}{}^2 \qquad (9)$$

factor and a_{1g} *etc.* are the constants of equation (8) divided by ΔE. Since the intensities of the various vibronic bands are additive, we may describe the integrated intensity of the $Q(1,0)$ region by a general equation of the form (10).

$$D_{Q(1,0)}/D_{B(0.0)} = A\sin^2\alpha + B\cos^2 2\alpha + C \qquad (10)$$

Thus equation (10) represents our basic result for cases in which the vibronic bands cannot be resolved. However, equation (9) presents an interesting possibility. Recalling that Gouterman *et al.*[10,11] have shown that negative A terms result from the vibronic coupling due to b_{1g} and b_{2g} modes, we see from equation (9) that the sign of the m.c.d. A term, together with the intensity variation with α, is

* See ref. 3 for state nomenclature. Additionally, a superscript zero indicates a matrix element evaluated at the equilibrium nuclear position, except when it appears as a state label. For instance, $|Q_x{}^0\rangle$ refers to the Q_x state in a specific reference porphyrin in which the configuration interaction parameter α is zero, while $|Q_x\rangle^0$ refers to the Q_x state for any porphyrin at the equilibrium geometry.

† If the potential surface for the normal mode ξ_r is harmonic, the cross terms between the Franck–Condon terms and the vibronic terms vanish. The first term is symmetric, and the second antisymmetric, with respect to reversal in the phase of the normal mode ξ_r.

sufficient to determine the symmetry of the vibrations responsible for each vibronic band.

EXPERIMENTAL

The experimental conditions are given in ref. 1 together with data for the Q(0,0) band of magnesium and zinc octaethylporphyrin. In addition, we obtained zinc and palladium porphin from Professor M. Gouterman, and prepared palladium octaethylporphyrin from the neutral porphyrin (Professor H. H. Inhoffen) and palladium chloride (Fisher Scientific Company) by the method of Adler *et al.*,[23] recrystallizing twice from chloroform–methanol. The purity was checked by t.l.c. The spectra were measured at 77 K in either EPA (diethyl ether–isopentane–ethanol, 5 : 5 : 2 v/v) or in MCH–IP (methyl cyclohexane–isopentane, 1 : 4 v/v). The pertinent spectral parameters for the Q band were obtained by moment analysis [24] and are given in Table 1.

TABLE 1

Experimental spectral parameters

Compound	Solvent [a]	Temp. (K)	$A_{Q(0,0)}$ (βD^2) [b]	A_Q (βD^2) [b]	$D_{Q(0,0)}$ (D^2) [b]	D_Q (D^2) [b]	$D_{B(0,0)}$ (D^2) [b]
Magnesium octaethylporphyrin	n-Octane	295	7·58	10·33	3·18	9·67	123
	Ethanol	295	7·34	9·95	3·79	12·06	150
	EPA	295	6·81	8·97	3·21	12·07	153
	EPA	77	1·96	2·37	1·38	12·02	153
	EPA–pyridine	295	8·71	7·93	3·90	12·78	143
	EPA–pyridine	77	2·44	3·45	1·42	11·91	137
	MCH–IP	295	8·79	10·54	2·95	8·91	118
Zinc octaethylporphyrin	n-Octane	295	9·65	18·52	6·42	13·69	141
	Ethanol	295	9·32	16·10	4·74	13·14	152
	Pyridine	295	7·04	9·69	4·09	12·74	142
	EPA	295	8·27	13·90	4·00	11·62	128
	EPA	77	6·34	15·03	3·35	11·01	126
	EPA–pyridine	295	7·66	12·41	4·02	11·89	140
	EPA–pyridine	77	5·01	15·64	3·27	12·02	138
	MCH–IP	295	8·93	20·22	6·17	14·43	130
Palladium octaethylporphyrin	EPA	77	19·08	23·49	6·88	16·5	*c*
Zinc porphin [d]	EPA	77	0·24	1·63	0·45	8·45	*c*
	n-Octane	295	0·78	2·07	1·79	9·79	*c*
Palladium porphin [d]	MCH–IP	77	4·25	7·67	4·15	11·15	*c*
	EPA	77	5·4	10·8	4·40	12·40	*c*

[a] EPA–pyridine = diethyl ether–isopentane–ethanol–pyridine, 24 : 20 : 12 : 1 v/v. [b] β = Bohr magneton, D = Debye unit. [c] Not available. [d] Data normalized in an approximate way. See ref. 14 for details.

The fitting procedure [1,13,14] consisted of (i) fitting the Q(0,0) m.c.d. band to obtain the wing parameter and half-width, and (ii) fitting the vibronic components with these parameters, allowing the A values and frequencies to vary freely.

RESULTS AND DISCUSSION

The Theory section describes the application of the four orbital model to the calculation of vibronic intensities under the assumption that vibrational integrals are constant. Figure 1 shows a plot of the experimental values of $D_{Q(1,0)}/D_{B(0,0)}$ and of $A_{Q(1,0)}/D_{B(0,0)}$ *versus* the configuration interaction parameter α and a fit of the general equation (10) to these data. It is clear that absorption intensity in the Q(1,0) band is largely due to vibronic coupling and decreases with α or at least does not increase.

It is equally clear that positive A terms become more significant with increasing α. We may surmise that, since vibronic contributions to the A value of the Q(1,0) band which are due to vibronic borrowing tend strongly to cancel, the Franck–Condon contributions cause the increase in $|A_{Q(1,0)}/D_{B(0,0)}|$ with increasing α.

There exists a possibility that the vibronic bands may be assigned by a combination of the sign of the m.c.d. A terms and the intensity variation with α. A treatment similar to that of the previous section indicates

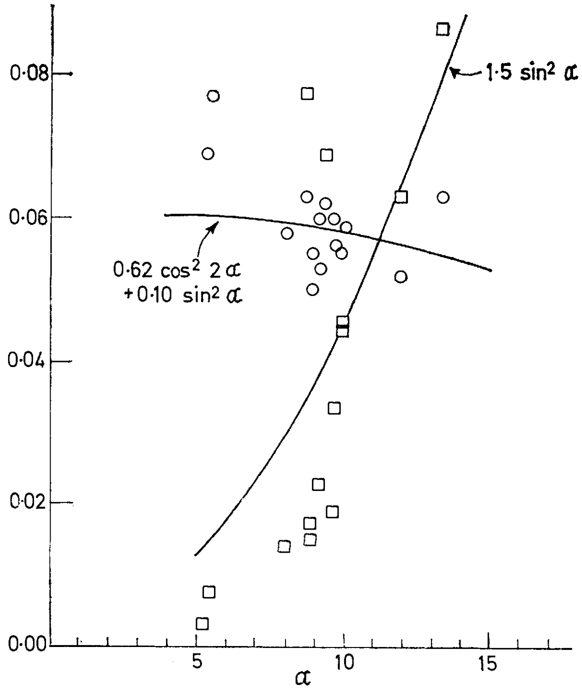

FIGURE 1 Magnesium and zinc octaethylporphyrin Q(0,0) spectral parameters *versus* configuration interaction parameter α: ○ $D_{Q(1,0)}/D_{B(0,0)}$; □ $A_{Q(1,0)}/D_{B(0,0)}$

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[23] A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2443.

[24] P. J. Stephens, R. L. Mowery, and P. N. Schatz, *J. Chem. Phys.*, 1971, **55**, 224.

that the magnetic moments of the vibronic bands are relatively unaffected by variations in α, primarily because the $Q(0,0)$ band has a large magnetic moment. Thus, we expect the $|A/D|$ values for the individual

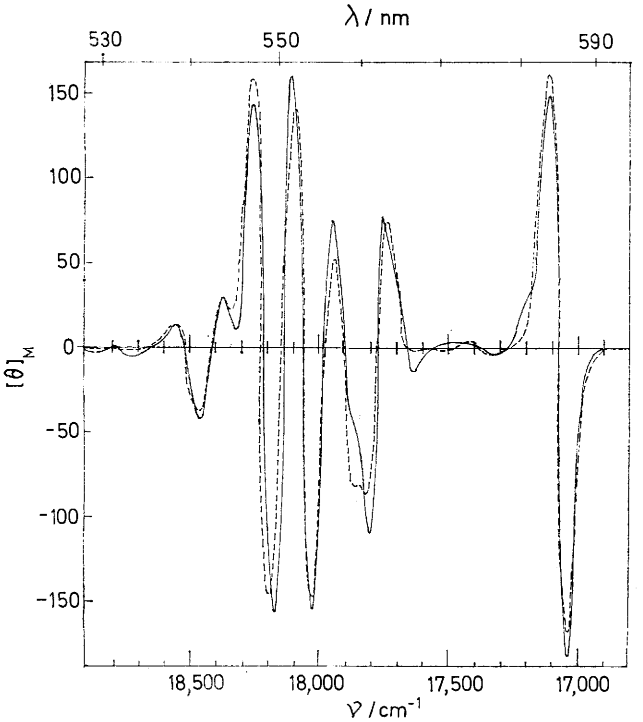

FIGURE 2 The m.c.d. spectra (experimental ——, fitted – – – – of magnesium octaethylporphyrin in EPA at 77 K

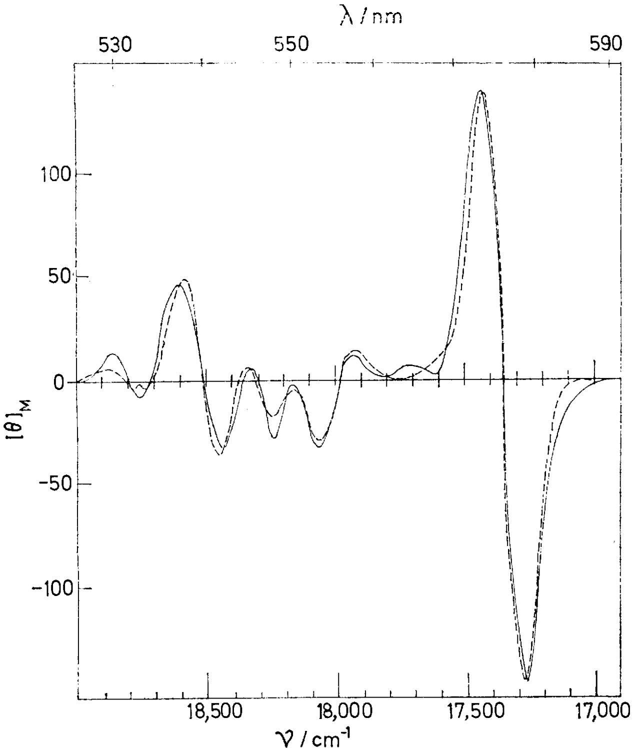

FIGURE 3 The m.c.d. spectra (experimental ——, fitted – – – –) of magnesium octaethylporphyrin in MCH–IP at 77 K

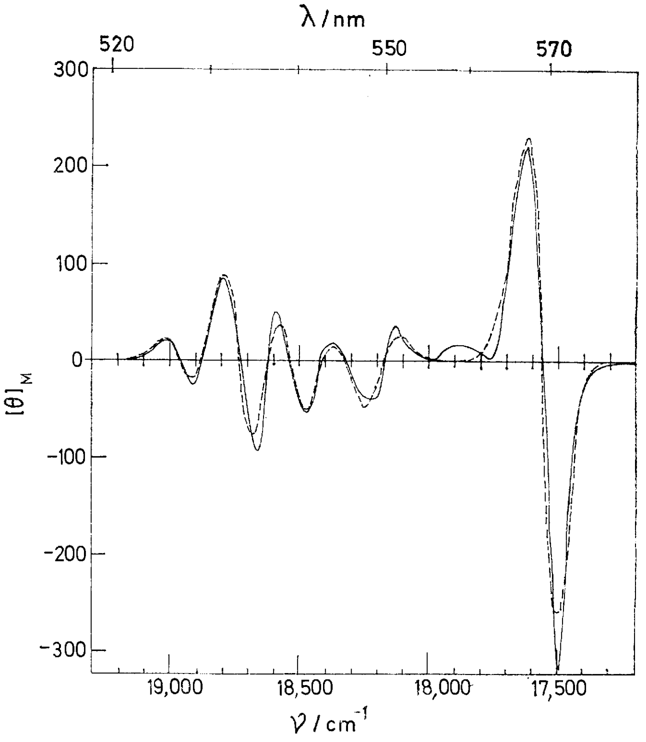

FIGURE 4 The m.c.d. spectra (experimental ——, fitted – – – –) of zinc octaethylporphyrin in EPA at 77 K

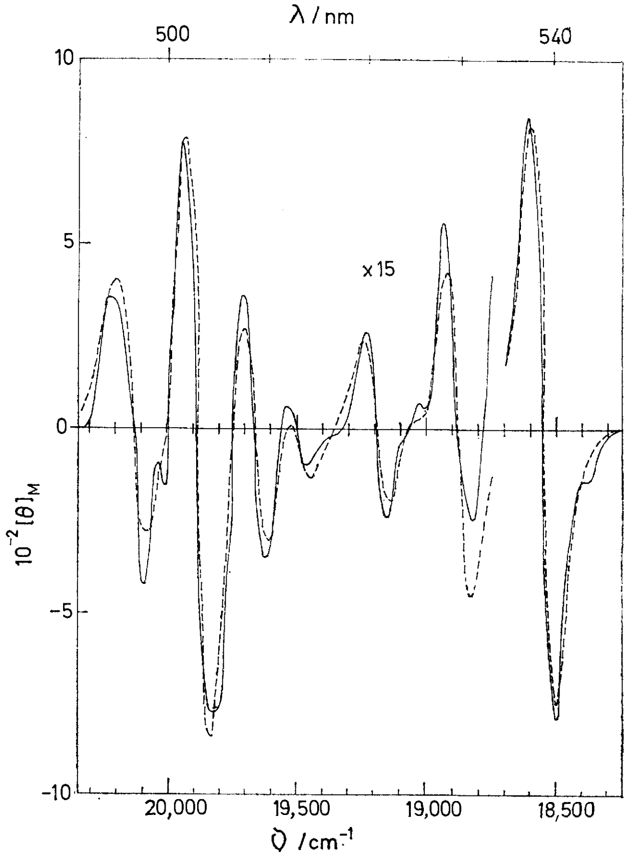

FIGURE 5 The m.c.d. spectra (experimental ——, fitted – – – –) of palladium octaethylporphyrin in EPA at 77 K

vibronic bands to be approximately constant and equal to that of the $Q(0,0)$ band so that the A values from the m.c.d. spectra reflect the D values in absorption. [Strictly speaking, it is necessary to allow for variations in the $Q(0,0)$ magnetic moment when different porphyrins are compared.]

The low temperature m.c.d. spectra of magnesium octaethylporphyrin in EPA and MCH–IP and of zinc and palladium octaethylporphyrin in EPA are given in Figures 2—5. The spectra are arranged in order of increasing α. All the spectra are reasonably well resolved, with the m.c.d. spectra of magnesium and palladium octaethylporphyrin in EPA being quite highly structured. Even though some features can be followed through the series, such as the first positive A term at $\nu_{Q(0,0)} + 300$ cm^{-1}, there is sufficient overlap as to render inspection fruitless. We fitted the spectra of Figures 2—5, assuming that the shape and halfwidth of each band is the same as that of the $Q(0,0)$ band and that the B value is zero. The results of those fits are indicated in Figures 2—5 with dashed lines and Table 2 gives the frequencies and A values. The intensity of the $Q(0,0)$ band, as reflected by the A value, varies over a large range (*ca.* 10). The corresponding range in the configuration interaction parameter α is from 5 to 17°.

TABLE 2

Vibronic A values and frequencies [a]

(a) Octaethylporphyrins (OEP)

Band	Vibrational symmetry	OEP^{2+}(PMMA) ν_i	OEP^{2+}(PMMA) A_i	MgOEP(EPA) ν_i	MgOEP(EPA) A_i	MgOEP(MCH–IP) ν_i	MgOEP(MCH–IP) A_i	ZnOEP(EPA) ν_i	ZnOEP(EPA) A_i	PdOEP(EPA) ν_i	PdOEP(EPA) A_i
A	$Q(0,0)$	0	1·9	0	2·0	0	6·2	0	6·4	0	19·1
B	a_{1g}^{FC}			302	0·05	300	0·1 [b]	254	0·38 [b]	324	0·75
	a_{2g}	501	0·5	604	0·07					485	0·11
C	b_{2g}	629	−0·75	697	−0·82	679	−0·83	623	−0·84		
D	a_{1g}			828	0·78	732	0·70	664	0·30	639	0·38
E, V	±	1002	−0·20	988	1·72	955	0·88	973	1·27	945	0·20
F	a_{1g}	1175	1·34	1143	1·76	1165	1·70	1166	2·15	1108	0·56
G	±	1258	−0·67	1343	−0·30						
H	a_{1g}^{FC}							1397	0·55	1330	1·38
J	a_{1g}	1503	0·50	1443	0·19	1465	0·24			1486	0·21
K	a_{1g}									1574	0·63
	a_{1g}									1640	0·23

(b) Porphins (P)

Band	Vibrational symmetry	ZnP(EPA) ν_i	ZnP(EPA) A_i	ZnP (n-octane, 20 °C) ν_i	ZnP (n-octane, 20 °C) A_i	PdP(MCH–IP) ν_i	PdP(MCH–IP) A_i	PdP(EPA) ν_i	PdP(EPA) A_i
A	$Q(0,0)$	0	0·24	0	0·78	0	4·25	0	5·35
B	a_{1g}^{FC}	369	0·04	369	0·11	325	0·76	327	0·56
								383	1·04
	a_{2g}								
C	b_{2g}							725	−0·12
D	a_{1g}	789	0·20	788	0·34	805	0·38	838	0·49
E	+	874	0·08			~960	±		
V	−	1030	−0·19						
F	a_{1g}	1174	0·39	1150	0·46	1147	0·56	1120	0·65
G	+	1234	0·49	1220	0·18	1249	1·72	1220	1·05
G′	−					1284	−1·04		
H	a_{1g}^{FC}							1360	0·20
J	a_{1g}	1469	0·24			1487	0·61	1480	0·77
K	a_{1g}	1567	0·14	1564	0·15	1578	0·33	1570	0·40

[a] Frequencies are in cm^{-1}; A values are in βD^2. Unless explicitly stated, all spectra were taken at 77 K. [b] This band was not included in the fit. The A value is estimated.

We will use the band labels of ref. 14, in which a close correspondence between Shpol'skii absorption spectra and m.c.d. spectra was established, to discuss the individual vibronic peaks. Table 2(a) gives the band labels and the m.c.d. frequencies and A values for a series of octaethylporphyrins. Table 2(b) gives the corresponding values for zinc and palladium porphin.

Assignment of the vibronic bands through the use of the A values in Table 2, in conjunction with equation (9), was accomplished as follows. The sign of the m.c.d. band classifies the perturbing vibration as either a_{1g} or a_{2g} (positive A value) or b_{1g} or b_{2g} (negative A values). We may distinguish between a_{1g} and a_{2g} by noting that only Franck–Condon allowed a_{1g} based bands can increase with α. A positive A term that decreases with α is due to an a_{2g} mode. The vibrations responsible for negative A values may be distinguished by noting that A values due to b_{1g} modes decrease as $\cos^2 2\alpha$ while those due to b_{2g} modes are constant with respect to α.

The A values listed in Table 2 show that band A undergoes a tenfold increase in A value for octaethylporphyrins, and a twentyfold increase in porphins. Since this band is the $Q(0,0)$ band, it is only electronically allowed, and typifies Franck–Condon behaviour.

Band B exhibits behaviour similar to that of band A and thus may be confidently assigned as a Franck–Condon allowed vibronic band (a_{1g}^{FC}).

The unlabelled band at 501 in octaethylporphyrin dication, at 604 in magnesium octaethylporphyrin (EPA), and at 485 cm^{-1} in palladium octaethylporphin (EPA) is not observed in unsubstituted porphins; consequently, an a_{2g} assignment is not reliable.

Band C is consistently observed in the octaethylporphyrins and also in palladium porphin (EPA). Since band C has a negative A value, and is approximately constant with respect to α, we may assign its symmetry as b_{2g}.

Band D represents a special case in two ways. In the octaethylporphyrins the positive A values decrease somewhat with α. The reverse is true in the porphins. Further, the frequency of this band varies with metal. We tentatively assign band D as due to an a_{1g} vibration which gains intensity both by vibronic borrowing and by Franck–Condon overlap.

Bands E and V are a pair of closely overlapping positive and negative A terms, resolved only in zinc porphin (EPA) and by inference in palladium porphin [13] (MCH–IP). The intensity of the overlapped pair varies considerably in the octaethylporphyrins but does not appear to become more negative with α. Thus these bands appear to be vibronically allowed and are due to overlapping of a_{1g} or a_{2g} with b_{1g} or b_{2g}.

Bands F and J are similar to band D in that the positive A values increase in intensity in porphins and decrease in octaethylporphyrins with α. On this basis we assign bands F and J as due to a_{1g} vibrations, with both Franck–Condon and borrowed intensity.

The situation with respect to band G is somewhat confused. Magnesium octaethylporphyrin (EPA) and the dication show negative A terms, but the negative A term for the magnesium octaethylporphyrin (EPA) appears in the band H frequency region (*ca.* 1375 cm^{-1}). Since we observe two positive A terms in the m.c.d. spectrum of palladium porphin (EPA), as well as the negative A term in the other porphyrins, we may conclude that three vibronic bands are present in this spectral region. Band H appears to be Franck–Condon in nature and hence $a_{1g}{}^{FC}$, but the symmetries of the negative and other positive bands are not clear.

Band K shows a positive A term which increases in intensity with the configuration interaction parameter α, although not in the ratio of the $Q(0,0)$ band. We thus assign this band as due to an a_{1g} mode, but having appreciable vibronically borrowed intensity.

Comparison with Previous Results.—We have compared our results with those obtained by Raman [25,26] and resonance Raman spectroscopy [15] in Table 3. Even though these results are not obtained on the same compounds, or even in the same electronic states, we might expect a general correlation between the results of these three methods. They share common selection rules, Raman peaks being allowed by a_{1g}, b_{1g}, or b_{2g} vibrational modes and the resonance Raman peaks and m.c.d. peaks being allowed by a_{1g}, a_{2g}, b_{1g}, and b_{2g} vibrations. Indeed, we find a general correlation of all three methods. In comparing Raman and resonance Raman, we note that the a_{2g} resonance Raman peak at 1584 cm^{-1} is not observed in normal Raman, as is proper. In the cases where an a_{2g} mode is observed to have anomalous polarization in resonance Raman, implying an accidental degeneracy with a_{1g}, b_{1g}, or b_{2g} modes, there is a peak observed in normal Raman. Thus the two Raman methods are in general agreement.

The m.c.d. spectra can be correlated with the results of both Raman methods. Of special interest is the

TABLE 3

Vibrational frequencies and symmetries [a]

Band	Shpol'skii frequencies (cm^{-1}) PdP[14]	Raman frequencies (cm^{-1}) CuOMP [25]	NiOMP [25]	PdOEP [26]	M.c.d. frequencies (cm^{-1}) and assignment MOEP	MP	Symmetry	Resonance Raman frequencies (cm^{-1}) polarization, and assignment [b] Ferrocytochrome c[14]		Composite assignment
B	378				300	360	$a_{1g}{}^{FC}$			$a_{1g}{}^{FC}$
C	700	752	752	748	623—697	725	b_{2g}	752dp	b_{1g} or b_{2g}	b_{2g}
D	766	686	687	660	828—639	789—838	$a_{1g}{}^{FC} + a_{1g}$ or a_{2g}	692p	a_{1g}	a_{1g}
E	960	957br	958br	1025	980	960	± Overlap	Solvent interference		a_{1g} or a_{2g} and b_{1g} or b_{2g}
F	1134	1138	1162		1160	1140	$a_{1g}{}^{FC} + a_{1g}$ or a_{2g}	1129ap	$a_{2g} + a_{1g}$ or b_{1g} or b_{2g}	$a_{1g} + a_{2g}$
								1174dp	b_{1g} or b_{2g}	b_{1g} or b_{2g}
				1219				1230dp	b_{1g} or b_{2g}	b_{1g} or b_{2g}
G,G′	1214	1236br 1310	1246 (2 shoulders)		1300	1250	± Overlap	1312ap	$a_{1g} + a_{2g}$ or b_{1g} or b_{1g}	$a_{2g} + b_{1g}$ or b_{2g} b_{2g}
H	1353	1365			1350	1360	$a_{1g}{}^{FC}$	1362p	a_{1g}	$a_{1g}{}^{FC}$
I	1440	1414						1399ap	$a_{2g} + a_{1g}$ or b_{1g} or b_{2g}	$a_{2g} + a_{1g}$ or b_{1g} or b_{2g}
J	1508			1453	1480	1480	$a_{1g}{}^{FC} + a_{1g}$ or a_{2g}	1483p	a_{1g}	a_{1g}
								1548dp	b_{1g} or b_{2g}	b_{1g} or b_{2g}
								1584ip	a_{2g}	a_{2g}
K	1599	1582	1592	1566	1574	1565	$a_{1g}{}^{FC} + a_{1g}$ or a_{2g}	1584ip 1594p	a_{2g} a_{1g}	a_{2g} a_{1g}

[a] Abbreviations for porphyrin names are: palladium porphin (PdP), copper octamethylporphin (CuOMP), nickel octamethylporphin (NiOMP), palladium octaethylporphin (PdOEP), metallo-octaethylporphin (MOEP), and metalloporphin (MP). [b] Abbreviations are: polarized (p), depolarized (dp), inverse polarization (ip), and anomalous polarization (ap).

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[25] K. N. Solovyov, N. M. Ksenofontova, S. F. Shkirman, and T. F. Kachura, *Spectroscopy Letters*, 1973, **6**, 455.

[26] H. Bürger, K. Burozyk, J. W. Buchler, J. H. Fuhrkop, F. Höfler, and B. Schrader, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 171.

observation of apparent accidental degeneracies in the normal Raman spectra (peaks E and V and peaks G and G′) in regions where the m.c.d. has overlapping positive and negative bands.

Since the polarizations of the resonance Raman peaks allow assignment of the vibrational symmetries, we can compare these methods in more detail. Spiro and Strekas [15] found that some of the resonance Raman bands had mixed symmetries (bands F, G and G′, and I). We found band F to have both Franck–Condon and borrowed intensity. We could interpret this result as the overlap of a peak based on an a_{1g} mode giving the Franck–Condon character and another based on an a_{2g} mode giving the borrowed intensity. Bands G and G′ show overlap of positive and negative A terms in m.c.d. and anomalous polarization in resonance Raman. The combination of selection rules indicate an a_{2g} based band overlapped by one based on b_{1g} or b_{2g} modes. Band I is not observed in m.c.d., presumably due to spectral overlap from the nearby band H. However, we may anticipate an anomalously polarized resonance Raman band in the region of peaks E and V a region now obscured by a solvent peak in the resonance Raman spectrum.

Band C represents a questionable correlation, in that the frequencies do not match well. We make the correlation because Spiro and Strekas report no other depolarized bands in this region. We assume that the mismatch in frequency is related to the fact that Spiro and Strekas do not report observing this band in ferrocytochrome c. If this is not the case, and the negative m.c.d. band in fact correlates with the polarized band at 692 cm^{-1} in the resonance Raman spectra (a_{1g}), then the two spectral methods are in contradiction. Further studies, using both techniques on the same compound, are required.

In summary, we have obtained evidence for appreciable Franck–Condon intensity in the $Q(1,0)$ band of several porphyrins, even though the major part of the intensity is due to vibronic borrowing. The variation in the intensity of the individual vibronic peaks has been used to obtain a tentative assignment for the vibrations responsible for these peaks, and comparison with results obtained by resonance Raman spectroscopy shows a general agreement.

We thank the National Institutes of Health and the National Science Foundation for partial support of this work. We thank Professor M. Gouterman for discussions and the samples of zinc and palladium porphyrin. We also thank Professor H. H. Inhoffen for his donation of octaethylporphyrin, and the Stanford Center for Information Processing for their donation of computer time.

[4/519 *Received*, 15*th March*, 1974]