Magnetic Circular Dichroism Studies. Part 45.[1] A Comparison between the Magnetic Circular Dichroism and Shpol'skii Spectra of Palladium, Zinc, and Magnesium Porphin

By **Günter Barth, Robert E. Linder, Nada Waespe-Sarcevic, Edward Bunnenberg,** and **Carl Djerassi,*** Department of Chemistry, Stanford University, Stanford, California 94305, U.S.A.
Yvonne Jones Aronowitz and **Martin Gouterman,** Department of Chemistry, University of Washington, Seattle, Washington 98105, U.S.A.

Eleven vibronic bands have been identified by curve fitting procedures in the low temperature m.c.d. spectra of palladium, zinc, and magnesium porphin. These bands correspond closely to the predominant lines in the Shpol'skii spectra, although differences in complexation states exist between the glass and polycrystalline matrices. Based upon the sign of the m.c.d. A terms and their intensity changes with changes in the oscillator strength of the $Q(0.0)$ band all vibronic bands could be assigned to a_{1g}, a_{2g}, b_{1g}, and b_{2g} modes. The $Q(0.0)$ band in magnesium porphin is of very low intensity and exhibits an A term of opposite sign compared to that reported as yet for other metallo porphins.

MAGNETIC circular dichroism (m.c.d.) spectroscopy has been of significant value in assisting the assignment of vibronic bands within electronic transitions of forbidden character, since the sign of the corresponding m.c.d. band is determined by the symmetry of the particular vibronic mode and the electronic state from which intensity is gained through vibronic coupling. Examples for these applications have been the $n \rightarrow \pi^*$ transition in ketones[2] and the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition in benzene.[3]

The requirement that the transition is of forbidden character is however not a necessary one since even in allowed transitions nontotally symmetric vibrations may contribute significantly to the observed absorption intensity.[4] Such a situation exists in metalloporphyrins for the lowest $A_{1g} \rightarrow E_u{}^1$ transition (the Q band) which although not forbidden by symmetry rules, can be of low oscillator strength and gains intensity through vibronic borrowing from the next higher allowed $A_{1g} \rightarrow E_u{}^2$ transition (the Soret band). As Perrin and Gouterman[5] have pointed out, nontotally symmetric vibrations of b_{1g} and b_{2g} symmetry are expected to exhibit m.c.d. A terms of sign opposite compared to the A term of the $Q(0,0)$ band.† This prediction has been verified experimentally in a series of porphyrin dications[6] and zinc and magnesium octaethylporphyrins[7] where at least one negative signed A term at ν_0 *ca.* +620—690 cm^{-1} could be located by curve fitting procedures.

Since the $Q(0,1)$ band is comprised of a large number of vibronic bands, as seen in the quasi-line Shpol'skii and single crystal spectra, the question remained as to the accuracy with which these bands can be identified in a low resolution spectrum such as is obtained in a glass matrix at liquid nitrogen temperatures where the half bandwidth is typically in the order of 100—200 cm^{-1}.

It is therefore the purpose of the present publication to make a detailed comparison between low temperature m.c.d. and Shpol'skii spectra on a set of compounds that appear to be mostly suited for this purpose and then to make symmetry assignments to the identified vibronic bands based on the sign of the m.c.d. A terms and their intensity changes with changes in the dipole strength of the $Q(0,0)$ band. Palladium porphin (PdP), zinc porphin (ZnP), and magnesium porphin (MgP) have been chosen since their Shpol'skii spectra have been reported and discussed in quite some detail,[8-12] even though some differences exist in the complexation state of the absorbing species in diethyl ether–isopentane–ethanol glass and n-octane polycrystalline matrix.

EXPERIMENTAL

The m.c.d. spectra were measured on a JASCO J-40 circular dichrometer equipped with an electromagnet which is capable of producing field strengths up to 15 kG.[13] The low temperature measurements were carried out in a jacketted brass cell of 0.8 cm pathlength that could be cooled with cold nitrogen gas. The temperature was monitored with a thermocouple. The absorption spectra were taken with a Cary 14M spectrophotometer. The m.c.d. spectral data, four points per nm, were directly transferred to a Nova-840 computer interfaced to the instrument.

In order to obtain as accurate a comparison as possible with a highly resolved Shpol'skii spectra the m.c.d. instrument was calibrated with a Fabry–Perot interferometer using a solution of holmium oxide in 1.4N-perchloric acid as

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† A normal or positive A term is one which exhibits a positive ellipticity at shorter wavelengths, such as the $Q(0,0)$ band in most metalloporphins.

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the primary standard.[14] The accuracy in wavelength is estimated to be better than 0.1 nm.

Palladium, zinc, and magnesium porphin were obtained by procedures described in the literature [15,16] and subsequently purified by chromatography on silica gel or aluminum oxide. Saturated solutions in EPA (diethyl ether–isopentane–ethanol 5 : 5 : 2 v/v) were prepared by stirring for several hours and their concentration determined from the optical density in the Soret region using the following extinction coefficients which correspond closely to those given in the literature: [17] PdP, ε_{386} 117 600, ZnP, ε_{397} 178 800, and MgP, ε_{397} 430 800 l mol^{-1} cm^{-1}. According to these values the solutions in EPA were of the following concentrations: PdP 1.96×10^{-6}, ZnP 3.91×10^{-6}, and MgP 2.03×10^{-5}M.

Fitting Procedure.—The fitting procedure was analogous to the one described in ref. 6, *e.g.* each individual m.c.d. band is determined by five parameters: $\Delta\nu$ the half bandwidth, ν_i the centre frequency, A_i the m.c.d. A value, B_i the m.c.d. B value and a, the wing parameter (if $a = 0$, the curve is a Gaussian, and if $a = 1$ the curve is a Lorentzian shapefunction). For the corresponding absorption bands A_i is set to zero and D_i, the oscillator strength, takes the place of B_i. The explicit expressions are:

$$[\theta]_M/\nu = -33.53 \sum_i [A_i f_0'(\nu_i) + B_i f_0(\nu_i)]$$

and (1)

$$\varepsilon/\nu = 108.9 \sum_i D_i f_0(\nu_i)$$

where

$$f_0(\nu_i) = \frac{[1 + 4(2^{a^2} - 1)(\nu - \nu_i)^2/\Delta\nu^2]^{-(1/a)^2}}{\Delta\nu/2[\pi/2^{a^2} - 1]^{1/2}\dfrac{\Gamma[(1/a^2) - 1/2]}{\Gamma(1/a^2)}}$$

Γ(x) is the gamma function, $[\theta]_M$ the magnetic molar ellipticity expressed in deg. cm^2 dmol^{-1} G^{-1}, and ε the molar extinction in units of l cm^{-1} mol^{-1}. The half bandwidth and the wing parameter were determined by fitting the Q(0,0) band separately and the Q(0,1) region was fitted holding these two parameters constant and letting ν_i and A_i or D_i vary freely. The m.c.d. B value was consistently found to be very small in magnitude and in order to reduce the ambiguity in fitting the Q(0,1) region of the m.c.d. spectrum it was set to zero. The number of bands was increased until a satisfactory fit was obtained, *e.g.* when addition of further bands leads to coincidence of two or more bands in the obtained fit.

RESULTS AND DISCUSSION

Complexation States.—Before discussing the fitting results and making comparisons with the Shpol'skii data it is relevant to investigate the question of the complexation states in which the several metalloporphins exist, since it has been shown in a previous publication [18] that this depends crucially on the temperature and the type of solvent used.

In the case of PdP (Figure 2) the situation appears to be particularly simple and it can be assumed with reasonable certainty that complexation does not occur, *i.e.* the palladium exists only in the four co-ordinate state. This is supported by the observation that no spectral changes occur when a polar solvent like methanol is used instead of a nonpolar one like n-octane other than a small blueshift of 1.5 nm. In addition, no further changes are observed on lowering the temperature to 77 K besides a band sharpening and a small blueshift of 80 cm^{-1}. A comparison with the Shpol'skii and single crystal spectra which were obtained in n-octane [8,9,11] should therefore be unaffected by the choice of the solvent. EPA has been chosen as solvent in this study solely for experimental reasons since particularly PdP dissolved very poorly in hydrocarbon solvents.

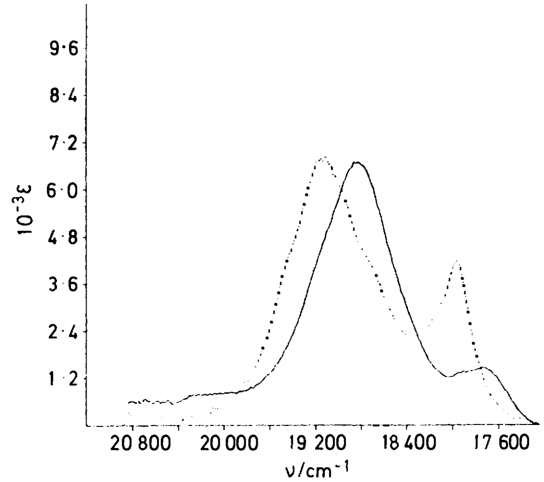

FIGURE 1 Absorption spectra of zinc porphin in methylcyclohexane–methylcyclopentane (1 : 1) (– – – –) and after addition of 0.1% methanol (——)

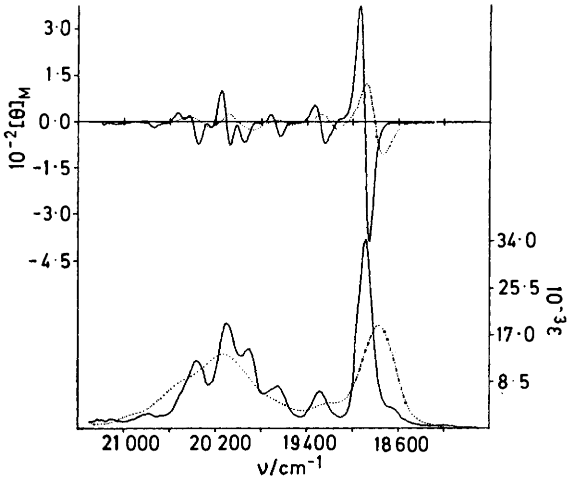

FIGURE 2 M.c.d. and absorption spectra of palladium porphin in EPA at room temperature (– – – –) and 77 K (——)

For ZnP (Figure 3) the situation is quite different and similar to the one discussed for zinc octaethylporphin in ref. 18 in that the central metal can easily accept a

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fifth ligand supplied by the solvent. The spectral changes associated with the transformation from the four to five co-ordination state are demonstrated in Figure 1 which shows the absorption spectrum of ZnP in n-octane and n-octane containing 0.1 vol % methanol.

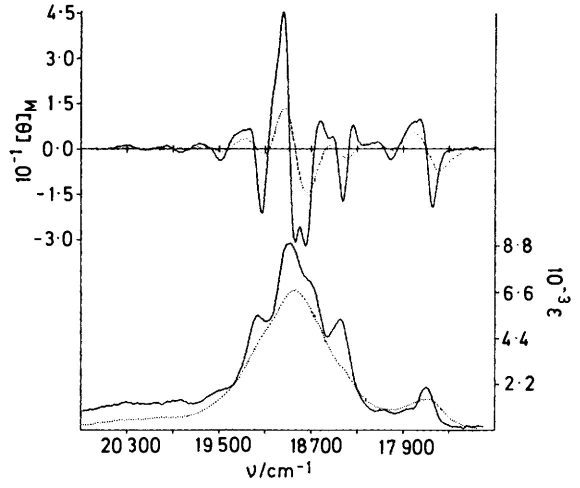

FIGURE 3 M.c.d. and absorption spectra of zinc porphin in EPA at room temperature (– – – –) and 77 K (——)

The whole Q band is shifted by 300 cm^{-1} to the red and the extinction coefficient of the Q(0,0) band is diminished from 4 200 to 1 400. A similar spectral change is observed when a solution of ZnP in methylcyclohexane–methylcyclopentane is cooled from room temperature to 77 K, presumably due to the presence of small amounts of water in the solvent mixture which we were unable to remove even after careful drying over sodium wire and molecular sieve. The m.c.d. and absorption spectra shown in EPA in Figure 3 are therefore those of the five co-ordinate ZnP where the fifth ligand is either ethanol or diethyl ether. Judging from the position of the Q(0,0) band in the Shpol'skii spectra [8,9,12] and the intensity distribution between the Q(0,0) and Q(0,1) bands, it appears that the absorbing species is the uncomplexed one. This is quite surprising since it was pointed out in ref. 8 that the spectrum had been obtained even when nonspecially dried n-octane had been used. It thus appears that when ZnP is trapped inside a crystalline octane matrix, the four co-ordinate species predominates.

A similar situation exists for MgP (Figure 4), which is reported to form four, five, and six co-ordinate species depending on the basicity of the ligand and the temperature. Recent work from Leiden [18a] indicates that for MgP in ' pure ' n-octane, the resulting spectrum is due to a mixture of species which have scavenged various fifth ligands from the medium (or perhaps from the original synthesis). This same explanation probably accounts for the very similar spectra shown by so-called four-co-ordinate MgTPP and five co-ordinate MgTPP reported in early studies [18b] and for the similarity of the Shpol'skii spectrum origin (17 419 cm^{-1}) for MgP in n-octane reported by Gradjushko *et al.*[9] and our own origin in EPA at room temperature (Figure 4). Going back to our recent work on MgOEP (magnesium octaethylporphin),[18c] the frequency shift reported between so-called four-co-ordinate MgOEP in octane and four-co-ordinate ZnOEP in octane is 380 cm^{-1}; but between five-co-ordinate MgOEP in ethanol and five-co-ordinate ZnOEP in ethanol, the shift is only 180 cm^{-1}. Other comparisons between wavelengths of various MgOEP and ZnOEP species reported earlier (ref. 18*c*, Table), suggest, in light of the recent Leiden report,[18a] that the species identified as four-co-ordinate MgOEP complexes may have actually been five-co-ordinate. Thus MgP complexes shift from five to six co-ordinate, whereas ZnP complexes shift from four to five co-ordinate. Perhaps heroic efforts can produce true four-co-ordinate MgP.

For the subsequent comparison between the m.c.d. curve fitting results and the Shpol'skii data it is therefore important to consider the effects of differences in complexation states; while the frequencies of the various vibrational modes are not expected to be influenced strongly by the presence or absence of additional ligands, their intensity distribution certainly is.

Comparison between M.c.d. and Shpol'skii Data.—Table 1 lists the Shpol'skii frequencies of PdP as given in ref. 8 together with their relative intensities. The frequencies obtained from the m.c.d. spectrum by curve fitting are listed in Table 2. Several correspondences to the m.c.d. vibronic bands are immediately obvious: *e.g.* 383 (386), 774 (786), 1 058 (1 043), 1 065 (1 066), 1 206 (1 205), 1 357 (1 365), and 1 486 (1 517) cm^{-1}, where we have put the corresponding Shpol'skii frequencies (Table 1) in parentheses. This assignment is also supported by the intensity distribution of these bands in both spectra. The assignment is however not so clear with respect to the m.c.d. bands at 909 and 1 101 cm^{-1} which could be related to the bands at 967 and 1 141 cm^{-1} in the Shpol'skii spectrum, although the

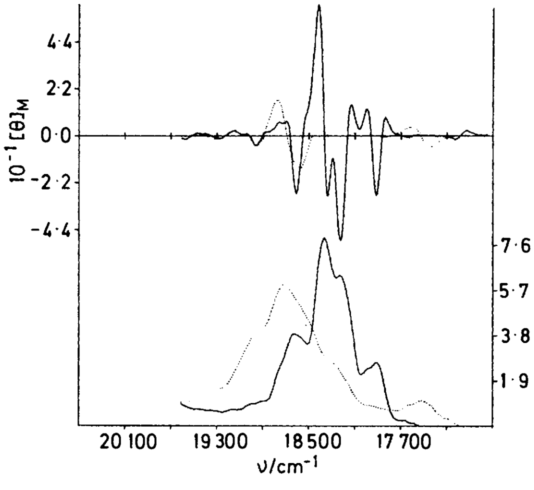

FIGURE 4 M.c.d. and absorption spectra of magnesium porphin in EPA at room temperature (– – – –) and 77 K (——). Note disappearance of Q(0,0) at 77 K

frequency discrepancies are appreciable and also the intensity distribution is not in agreement with this correlation. However, since in the 900—1 200 cm^{-1} region the bands are very closely spaced so that the assignments of the Shpol'skii frequencies also presents difficulties[8] a better correlation can perhaps not be expected. All identified bands exhibit positive A terms with the exception of the band at 1 058 cm^{-1} which is of negative sign.

TABLE 1

Shpol'skii data for PdP, ZnP, and MgP

PdP[a]	ν_i/cm^{-1}	(Rel. intensities)	ZnP[b]	ν_i/cm^{-1}	MgP[c]	ν_i/cm^{-1}
18 834	0	(100)	17 960	0i	17 419	0
	265	(3)		178m		
	386	(24)		368m		
	786	(10)		717w		711m
				780m		771m
	967	(15)		973m		960m
	1 043	(5)		1 035m		1 036w
						1 108m
	1 066	(3)		1 165w		
	1 141	(13)				1 153i
	1 205	(20)		1 220i		1 235w
				1 305w		1 253w
	1 365	(5)		1 390w		1 299m
	1 517	(5)		1 500w		1 389m

[a] Data taken from ref. 8, only the bands with a relative intensity larger than 3 are listed. [b] Data taken from ref. 8, i = intense, m = medium, w = weak, bands listed as very weak have not been included. [c] Data taken from ref. 9, bands listed as very weak and extremely weak have not been included.

For zinc porphin correlation of the vibronic bands is complicated by the occurrence of a relatively large zero field splitting of 108 cm^{-1}, so that the assignments made in ref. 8 (Table 1) can only be regarded as tentative. Nevertheless, the general correspondence between the m.c.d. fitting results in Table 2 and the Shpol'skii data in Table 1 (given in parentheses) is good; *e.g.* 369 (386), 709 (717), and 1 377 (1 390) cm^{-1}. The most intense m.c.d. vibronic band at 1 185 cm^{-1} probably corresponds to the intense Shpol'skii band at 1 220 cm^{-1}. Furthermore the m.c.d. band at 1 001 cm^{-1} is probably a composite of the two bands occurring at 973 and 1 035 cm^{-1} in the Shpol'skii spectrum.

TABLE 2

Curvefitting results for Pd, Zn, and Mg porphin[a]

Symmetry	assignment	Palladium porphin ν_i/cm^{-1}	Palladium porphin A_i/β D^2	Palladium porphin A_iD$_i^{-1}/\beta$	Zinc porphin ν_i/cm^{-1}	Zinc porphin A_i/β D^2	Zinc porphin A_iD$_i^{-1}/\beta$	Magnesium porphin ν_i/cm^{-1}	Magnesium porphin A_i/β D^2	Magnesium porphin A_i : D$_i/\beta$
$Q(0,0)$		18 895	5.89	1.82	17 690	0.43	1.79	17 167	−0.06	
I	a_{1g}^{FC}	+383	0.96	1.66	+369	0.08				
II	b_{2g}				+709	−0.74	−2.96	+704	−0.15	−0.71
III	a_{1g}–a_{2g}	+774	0.52	1.13	+729	0.69	1.41	+777	0.21	1.00
IV	a_{1g}^{FC}	+909	0.13	0.16						
V	b_{1g}	+1 058	−0.59	−1.43	+1 001	−0.35	−0.80	+1 004	−0.21	−0.75
VI	a_{1g}–a_{2g}	+1 065	0.99	2.41	+1 063	0.39	1.08	+1 092	0.41	0.53
VII	a_{1g}–a_{2g}	+1 101	0.47					+1 161	0.25	0.43
VIII	a_{1g}–a_{2g}	+1 205	1.56	1.75	+1 185	1.04	1.39	+1 207	0.72	0.87
IX	b_{2g}				+1 377	−0.26	−0.72	+1 382	−0.18	
X	a_{1g}	+1 357	0.26							
XI	a_{1g}–a_{2g}	+1 486	0.94		+1 474	0.27	0.64	+1 487	0.17	
			ΣA_i 11.13	D 9.27		ΣA_i 1.55	D 3.25		ΣA_i 1.16	D 2.38

[a] β = Bohr magneton unit, D = Debye unit.

In the spectrum of MgP the correspondence between m.c.d. bands from Table 1 and Shpol'skii bands from Table 2 (given in parentheses) is: 704 (711), 777 (771), 1 004 (1 036), and 1 092 (1 108) cm^{-1}. The strongest band in the m.c.d. spectrum appears at 1 207 cm^{-1} whereas the most intense Shpol'skii band is located at 1 153 cm^{-1}. Another band at 960 cm^{-1} has no obvious counterpart in the m.c.d. spectrum, a similar situation as in ZnP, and it can be assumed that the intensity of this particular band is dependent on the complexation state and decreases with decreasing oscillator strength of the $Q(0,0)$ band.

The identification of negative m.c.d. A terms can furthermore be supported by comparing an m.c.d. spectra with the first derivatives of the corresponding absorption spectrum. If we assume that all individual bands have the same $A : D$ ratio in sign and magnitude and furthermore that contributions of B terms can be neglected we may write equation (2) since the first term

$$d\varepsilon/d\nu = 108.9[\sum_i D_i f_0(\nu_i) + \nu \sum_i D_i f_0'(\nu_i)] \qquad (2)$$

is of the order of $\Delta\nu_i/\nu$ times the second, we ignore it and write, substituting $2A_i/\mu$ for D_i, equation (3), where μ is the magnetic moment.

$$d\varepsilon/d\nu = \frac{217.8}{\mu} \sum_i \nu A_i f_0'(\nu_i) \qquad (3)$$

From equation (1), if we ignore B terms, we may write $d\varepsilon/d\nu = -6.5[\theta]_M/\mu$. Thus the shape of the m.c.d. spectrum should be very similar to that of the first derivative of the absorption spectrum. This comparison has been made in Figures 5—7 where, as can be seen, the major discrepancies between the two curves in each Figure occur at those frequencies at which negative A terms had been identified previously through curve fitting methods, *e.g.* at 19 750—19 900 cm^{-1} in PdP and 18 270—18 480, 18 560—18 700, and 19 040—19 200 cm^{-1} in ZnP and 17 760—17 900, 18 080—18 240, and 18 480—18 600 cm^{-1} for MgP.

The lower amplitude of the first derivative compared to the experimental m.c.d. spectrum is a direct consequence of the larger halfband width of the absorption bands, an observation we have made previously on a number of other metalloporphyrins,[18c] porphyrins, dications,[6] and dianions.[19] In the case of PdP the half-band width of the $Q(0,0)$ band at 77 K is 109 cm^{-1} in the m.c.d. and 150 cm^{-1} in the absorption spectrum. Since the amplitude of an m.c.d. A term is inversely proportional to the square of the halfband width the first derivative curve has to be multiplied by 1.9 which brings it to within 15% correspondence with the m.c.d. spectrum.

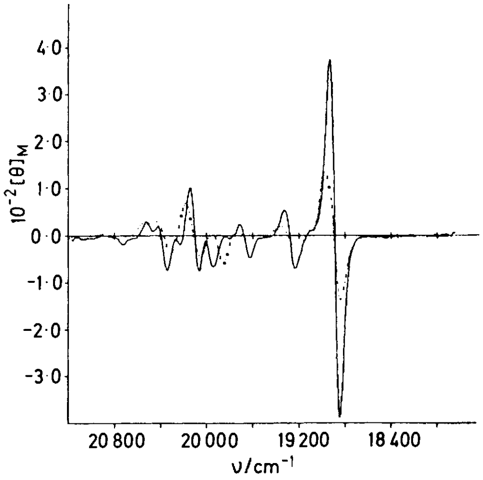

FIGURE 5 M.c.d. spectrum (——) and first derivative of the absorption spectrum (– – – –) of palladium porphin in EPA at 77 K

Summarizing these results, we have located a total of eleven vibronic bands [(I)—(XI), Table 2] three of which exhibit negative m.c.d. A terms. The assignments remain somewhat questionable in the 900—1 200 cm^{-1} region.

Comparison with Previous Results.—In comparing these results with those previously obtained for octaethylporphin dications $(OEP)H_4^{2+}$ [6] and its Mg, Zn, and Pd complexes (MgOEP, ZnOEP, PdOEP),[7] we will restrict ourselves only to those bands where a conclusion is least ambiguous, namely the b_{1g} and b_{2g} modes which exhibit negative A terms and the a_{2g} mode of largest intensity (band VIII in ZnP, MgP, and PdP).

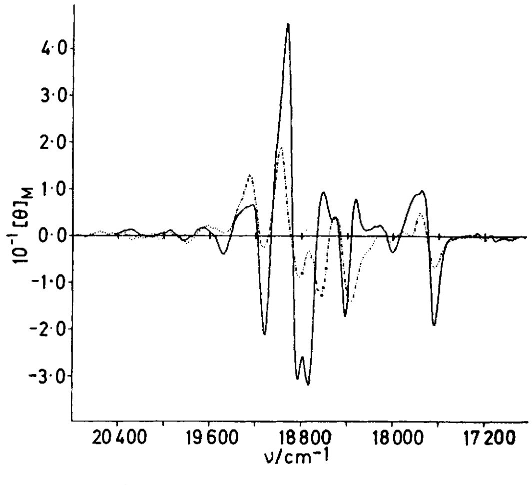

FIGURE 6 M.c.d. spectrum (——) and first derivative of the absorption spectrum (– – – –) of zinc porphin in EPA at 77 K

The lowest frequency b_{2g} mode was observed at 629, 697, and 623 cm^{-1} in $(OEP)H_4^{2+}$, MgOEP, and ZnOEP respectively at slightly lower frequency than the corresponding band (band II) in ZnP and MgP. Band V at 1 001—1 058 cm^{-1} in PdP, ZnP, and MgP was observed only in $(OEP)H_4^{2+}$ at 1 002 cm^{-1}, whereas band IX at 1 377—1 382 cm^{-1} was observed in $(OEP)H_4^{2+}$ and MgOEP at 1 258 and 1 343 cm^{-1} respectively. The most intense a_{2g} mode (band VIII) was observed at 1 175, 1 143, 1 160, and 1 330 cm^{-1} in $(OEP)H_4^{2+}$, MgOEP, ZnOEP, and PdOEP respectively. In addition band I, the Franck–Condon a_{1g} band, was also found as a relatively intense band at 324 cm^{-1} in PdOEP.

Symmetry Assignments.—In the D_{4h} point group vibronic species belonging to a_{1g}, a_{2g}, b_{1g}, and b_{2g} symmetry can contribute to the intensity of the $Q(0,1)$ band.[7] A distinction between them is possible in the following way. The a_{1g} and a_{2g} modes are expected to exhibit positive A terms; in addition, since the intensity of a_{1g} modes can come either through Franck–Condon overlap with $Q(0,0)$ or from vibronic borrowing from $B(0,0)$ (while the asymmetric modes can only come through the latter route), the intensity of some a_{1g} modes may parallel that of the $Q(0,0)$ band. The b_{1g} and b_{2g} vibrational modes will exhibit negative A terms; distinction between these two possibilities can be made by observing their intensity variations with changes in the oscillator strength of the $Q(0,0)$ band: b_{2g} modes are expected[7] to decrease in intensity with increasing intensity of the $Q(0,0)$ band whereas the intensities of the B_{1g} mode remains more or less unchanged.

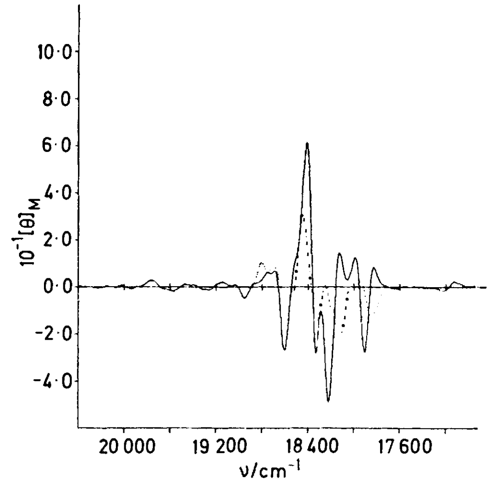

FIGURE 7 M.c.d. spectrum (——) and first derivative of the absorption spectrum (– – – –) of magnesium porphin in EPA at 77 K

The set of compounds chosen is ideally suited for such an analysis. PdP represents an example where the $Q(0,0)$ band is of high intensity (D 3.24) so that the transition is allowed in which case one would expect

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[19] G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *J.C.S. Perkin II*, 1974, 696.

considerable contribution from a_{1g}^{FC} modes within the $Q(0,1)$ region. On the other hand the $Q(0,0)$ band in MgP is of very low intensity and the transition is accidentally forbidden so that all intensity results from vibronic borrowing from the E_u^2 state. ZnP represents an intermediate case. Based on such a comparison the 383 cm^{-1} band (band I) in PdP is clearly based on an a_{1g}^{FC} mode since it is absent in the spectrum of MgP, and only weakly visible in ZnP; presumably this relates also to the bands of 909 and 1 357 cm^{-1} in PdP. Further unambiguous assignments can be made based on the sign of the m.c.d. A terms; bands II, V, and IX are therefore clearly non-totally symmetric b_{1g} and b_{2g} modes. Since band II and IX are not observed in the spectrum of PdP they can be assigned to b_{2g} modes. It should be pointed out however that both these bands could be obscured by the close proximity of the positive A terms of bands VI and X which have been assigned to Franck–Condon modes and are therefore particularly intense in PdP. The identification of the a_{1g} or a_{2g} modes which borrow intensity from the Soret band follows then quite logically; *e.g.* all bands with positive A terms in the spectrum of MgP must be of these symmetries, these are the bands III, VI—VIII, and XI. In summary, from the eleven vibronic bands identified in Pd, Zn, and Mg porphin three belong to a_{1g}^{FC} modes, five to a_{1g}–a_{2g} modes, one to a b_{1g} mode, and two to b_{2g} modes, respectively.

$A : D$ *Ratios*.—Although one of the initial aims of this investigation was to obtain reliable $A : D$ ratios for each vibronic band, the curve fitting results of the low temperature absorption spectra make such a determination ambiguous. The main reason is that the halfband width is *ca.* 30% larger in the absorption than in the m.c.d. spectrum.

Therefore the fitting results were not unique and small changes in frequencies alter the intensity distribution among the various bands significantly. The $A : D$ ratios listed in Table 2 are only those for which a reasonable agreement between the frequencies in both the m.c.d. and absorption spectra exists. The $A : D$ ratios of the various bands varies quite significantly but, because of the uncertainties involved, the error margin is too large to draw any conclusions from these values. One exception is the Franck–Condon band at 383 cm^{-1} in PdP which is quite isolated from other vibronic bands, its $A : D$ ratio is found to correspond closely to the one for the $Q(0,0)$; *i.e.* 1.66 *versus* 1.82. Table 3 summarizes the results of the moment analysis for the Q band for Pd, Zn, and Mg porphin. In agreement with the results previously reported,[6,18c,19] the $A : D$ values for the entire band are considerably smaller than the $A : D$ values for the $Q(0,0)$ band alone. While we believe that this lower $A : D$ ratio in the $Q(0,1)$ region as compared to the $Q(0,0)$ band results from the presence of negative A terms, Jahn–Teller quenching of the magnetic moment remains a possibility and cannot be unambiguously excluded.

Discussion of Inverted A *Term for the* Q(0,0) *Band*.—Finally we wish to discuss the experimental observation of a sign inversion for the A term of the $Q(0,0)$ band in MgP. In a previous publication[6] we have made a similar observation in the case of porphin dication where the $Q(0,0)$ band is of very low intensity so that it could not be detected in the absorption spectrum but the corresponding m.c.d. spectrum exhibits a negative A term in the region where the $Q(0,0)$ band is expected to be located, based on the frequencies of the various vibronic bands. In the case of MgP, where we have identified eight vibronic bands and were able to correlate them with those of PdP and ZnP, the $Q(0,0)$ band can be predicted within quite narrow limits to be located at 17 180 cm^{-1} whereas the centre of the experimentally observed negative A term appears at 17 167 cm^{-1}. This close agreement seems to exclude the possibility that this m.c.d. band is due to a low frequency vibration and leaves little doubt that it is in fact the electronic origin of the Q band.

TABLE 3

Moment analysis for Pd, Zn, and Mg porphin[a]

	T/K	A/β D^2	B/β D^2 cm	D/D^2	AD$^{-1}/\beta$
ZnP	Ambient	2.47	0.63×10^{-3}	3.99	0.62
	77	2.00	0.16×10^{-3}	3.25	0.62
PdP	Ambient	6.48	0.33×10^{-2}	9.21	0.70
	77	3.09	0.20×10^{-1}	8.74	0.35
MgP	Ambient	1.82	0.81×10^{-3}	2.62	0.69
	77	0.99	-0.17×10^{-3}	2.38	0.42

[a] β = Bohr magneton unit, D = Debye unit.

The possibility of inverted A terms was earlier discussed.[20] The discussion makes clear that as long as the molecule has a four-fold symmetry axis, the $Q(0,0)$ band must maintain $A > 0$. This arises from the fact that C_4 (rotation by 90°) transforms the transition dipoles as in equations (4). If there is a four-fold axis,

$$\begin{aligned} C_4R_x\hat{\imath} &= \eta R_y\hat{\jmath} \\ C_4R_y\hat{\jmath} &= -\eta^{-1}R_x\hat{\imath} \end{aligned} \tag{4}$$

$\eta = 1$ and $A > 0$.[20] The studies reported here suggest that in EPA at 77 K MgP is six-co-ordinate; thus symmetry no longer requires $\eta = 1$. In fact it is quite reasonable that in the absence of a four-fold axis, η can become negative. That is, we can write equations (5)

$$R_x = (R + \Delta);\ R_y = (R - \Delta) \tag{5}$$

where R is the four-fold symmetric part and Δ is due to the lower symmetry. For small R_x, R_y it is quite reasonable that we may have $|\Delta| > |R|$ giving $\eta < 0$ and an inverted A term.

Conclusions.—We have been able to locate a total of eleven vibronic bands within the $Q(0,1)$ band of Pd, Zn, and Mg porphin by curve fitting of the m.c.d. spectra, and these frequencies are found to be in close agreement with the predominant bands in the quasi-line Shpol'skii spectra. Based upon the sign of the m.c.d. A terms and their intensity variations with changes in the oscillator strength of the $Q(0,0)$ band all of them can be assigned

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[20] A. J. McHugh, M. Gouterman, and C. Weiss, jun., *Theor. Chim. Acta*, 1972, **24**, 346; note that an opposite sign convention for A was used.

to the four possible symmetry species a_{1g}, a_{2g}, b_{1g}, and b_{2g}. As a result it was found that vibronic borrowing, which is the only mechanism by which the *Q* band gains intensity in MgP, still remains an important factor in the spectrum of PdP where a_{2g} and the b_{1g} modes contribute at least 50% to the total intensity of the *Q*(0,1) band even though it must be considered as an allowed transition. Furthermore, the previously[6] reported anomaly of a negative *A* term for the *Q*(0,0) band in porphin dication could be confirmed in the m.c.d. spectrum of MgP where again the *Q*(0,0) band is of very low intensity and exhibits a m.c.d. *A* term of negative sign.

Finally, there may be some point in comparing frequencies from resonance Raman (RR) data and frequencies we have derived from m.c.d.–Shpol'skii absorption data, albeit that the former refer to ground state vibrations and the latter to excited state vibrations. In Table 4 we have compared our frequencies from MgP, ZnP, and PdP with those of CuP found in resonance Raman studies.[21] Both RR and absorption intensity depend on the transition dipole between vibronic states, and vibrations that appear relatively strongly in Shpol'skii absorption are likely to be intense in RR. Qualitatively this is shown in Table 4, since there are 12 relatively intense RR lines compared to 11 deduced from m.c.d.–Shpol'skii. However, the only clear correspondences of RR (m.c.d.) are the 368 (376) cm^{-1} band and the 998 (909) cm^{-1} band. It also definitely appears that the a_{1g}, b_{1g}, and b_{2g} vibration frequencies are larger in the ground state (*i.e.* in RR) than in the excited state (*i.e.* from m.c.d.). This was predicted on theoretical grounds, since these modes gain intensity by coupling *Q* and *B* states.[20] Ultimately a clear correspondence between vibronically active modes as measured by the two spectroscopic techniques should prove possible.

TABLE 4

Comparison of m.c.d. excited state vibrations [a] and resonance Raman vibrations [b]

RR a_{1g}	RR a_{2g}	M.c.d. a_{1g}	M.c.d. a_{1g}–a_{2g}	RR b_{1g}–b_{2g}	M.c.d. b_{1g}	M.c.d. b_{2g}
368		376				
						704
732			760			
998		909				
			1 073	1 059	1 021	
			1 131			
			1 199	1 180		
	1 322			1 352		
1 370		1 357				1 380
			1 480	1 498		
1 562	1 587					
				1 631		

[a] Average of frequencies of Table 2. [b] CuP, weak or very weak lines omitted.[21]

This work has been supported by a grant from N.I.H. and a Public Health Services Research Grant. One of us (N. W.) wishes to thank the Stiftung für Stipendien auf dem Gebiete der Chemie, Switzerland, for scholarship support.

[6/848 *Received*, 3*rd May*, 1976]

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[21] A. L. Verma and H. J. Bernstein, *J. Chem. Phys.*, 1974, **61**, 2560.