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RESONANCE RAMAN SCATTERING
OF MESOPORPHYRIN IX DIMETHYLESTER IN SOLUTION

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ABSTRACT

Resonance Raman spectra of Mesoporphyrin IX dimethylester in solution were obtained using various wavelengths in the region of electronic band IV. Vibrational data, as well as variations in the depolarization ratios and the band intensities with excitation wavelengths were compared to those previously obtained for porphin. The new data provide confirmation of the existence of three, most probably purely electronic transitions in band IV of both Mesoporphyrin IX dimethylester and porphin.

RESUME

L'ester diméthylique de la mésoporphyrine IX (mesoPdme) est étudié en diffusion Raman de résonance par irradiation dans la bande IV du spectre d'absorption (entre 441,6 et 514,5 nm). Les auteurs discutent les fréquences des bandes de vibration observées, les variations de leur intensité et de leur taux de polarisation et les comparent à celles qu'ils ont obtenues précédemment pour la porphine. Ils mettent en évidence l'existence de trois zones de résonance dans la bande IV (vers 505, 470 et 459 nm) qu'ils attribuent, comme dans le cas de la porphine, à la présence de trois transitions électroniques pures. Enfin, ils montrent également que des résonances se produisent sur des sous-niveaux vibrationnels de l'une de ces transitions ainsi que sur certains de la bande III.

INTRODUCTION

In a recent study of porphin solutions by Resonance Raman (RR) scattering (1, 2) we suggested that three purely electronic transitions might occur in absorption band IV, in addition to the previously recognized vibrational sublevels of band III. We have now applied the same technique to band IV of Mesoporphyrin IX dimethylester (mesoPdme) (3), in an attempt to confirm the results obtained for porphin. The present article deals with a more detailed discussion and comparison of the existing vibrational and electronic data for porphin and mesoPdme.

EXPERIMENTAL

MesoPdme (Koch-Light), checked for purity by thin layer chromatography on Kieselguhr (4) and by ultraviolet and visible absorption spectra, was used without further treatment, dissolved in carbon tetrachloride or dimethyl formamide (DMF), and vacuum degassed. Concentrations were about $4 \cdot 10^{-4}$ M.

Spectroscopic methods, as well as treatment of spectral data - including corrections for reabsorption and spectral sensitivity of the apparatus - were identical to those used for porphin (1, 2).

Finally, absorption spectra of samples run in a series of Raman experiments did not show any noticeable irradiation effect.

RESULTS AND DISCUSSION

The visible absorption spectrum of mesoPdme is reproduced on figure 1, together with the positions of the irradiating wavelengths, including the 441,6 nm line of an He-Cd laser.

Figure 2 shows RR spectra of mesoPdme obtained under 472,7 nm illumination, in parallel and perpendicular polarizations.

Our spectra obtained under 488 nm illumination are in good agreement with the RR spectrum of solid mesoPdme recently published by Verma and Bernstein (5).

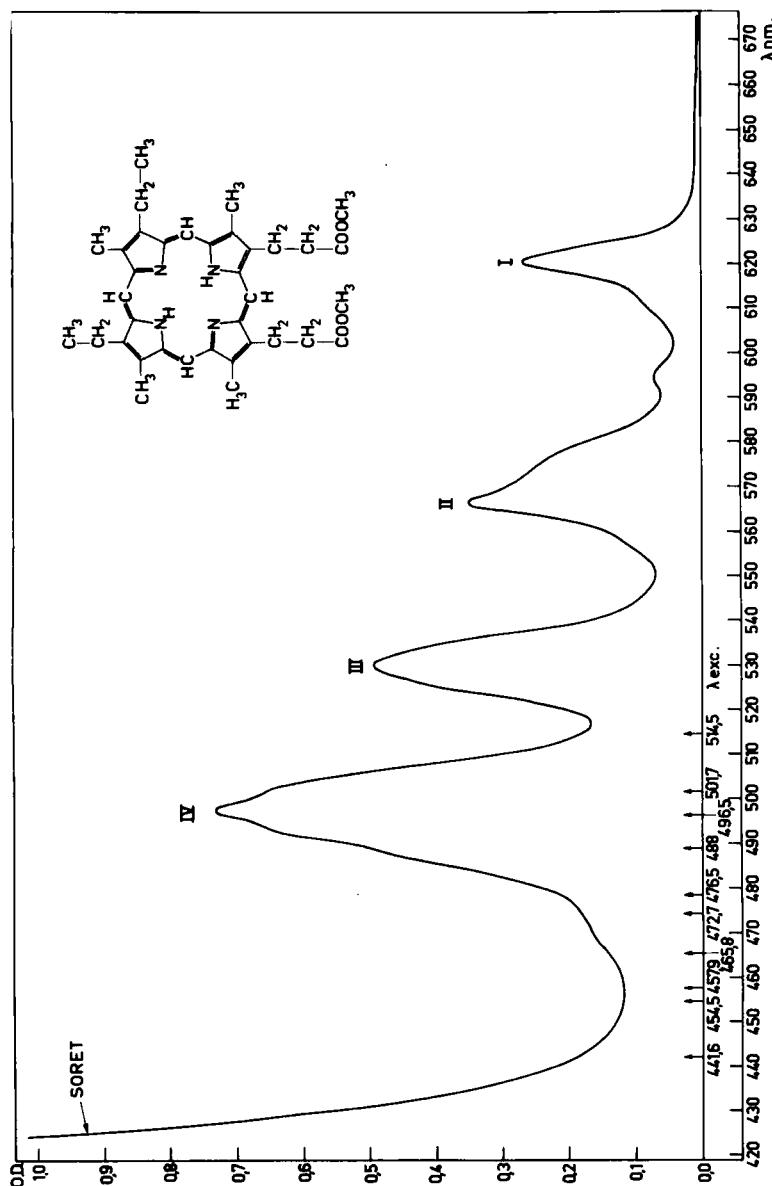


Figure 1 : Absorption spectrum of mesoporphyrin IX dimethyl ester in DMF (4 10^{-4} M, thickness 1 mm).
 λ_{exc} : irradiation wavelengths.

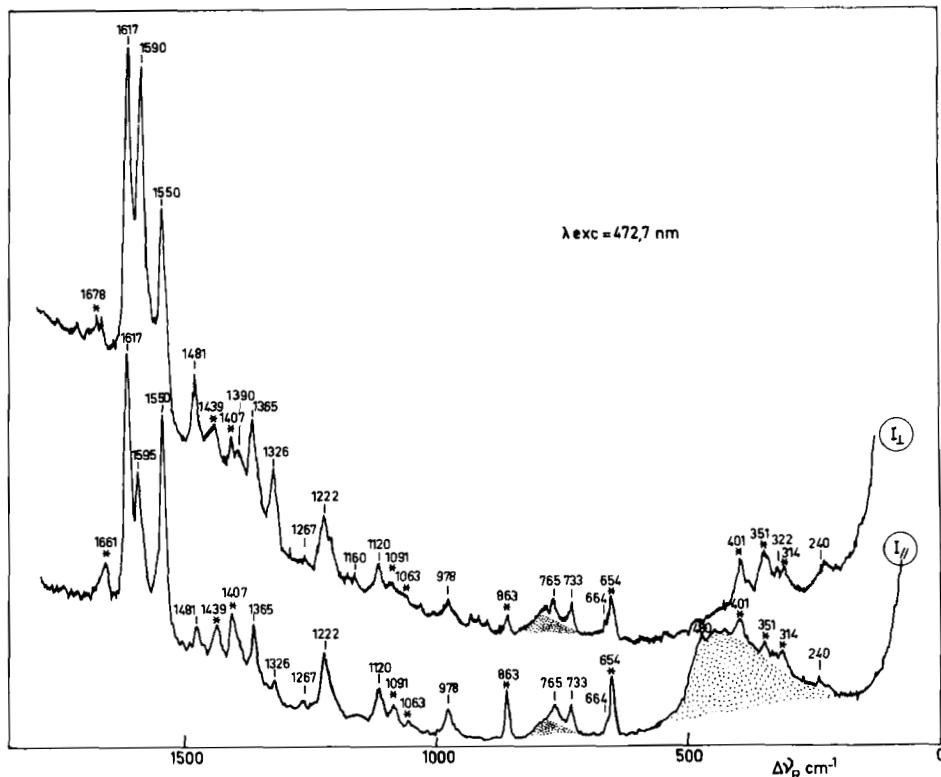


Figure 2 : RR spectra of mesoPdme in DMF at 472.7 nm. Dotted areas : Raman spectrum of the cell glass. * : DMF bands.

Vibrational frequencies

Table I indicates the vibrational frequencies observed for mesoPdme in the 0-1800 cm^{-1} region. A number of tentative correlations with RR frequencies of porphin in solution are proposed, based not only on the comparison of the observed frequencies, but also on the depolarization ratios found for the

TABLE I

MESOPORPHYRIN IX DIMETHYLESTER RR (this work)				PORPHIN RR (ref. I)			PP IX Fluo. (ref. 6)	PHEOPHYTIN RR (ref. 7) a	
$\Delta\nu_R$ cm ⁻¹	Pol. states, 442 to 515 nm	Relative intensity	Pol. state	$\Delta\nu_R$ cm ⁻¹	Relative intensity	Pol. state	$\Delta\nu_S$ cm ⁻¹	$\Delta\nu_R$ cm ⁻¹	$\Delta\nu_R$ cm ⁻¹
-	-	-	-	152	23	P	-	-	170
240	P-aP?-P	9	P?	-	-	-	240	255-x	250
322	P	8	P	309	50,5	P	-	300	298
-	-	-	-	386	ϵ	aP?	-	390-x	395-x
465?	-	ϵ	-	465	3	P	-	460	465
480	P	ϵ	P	490	2	P	-	490-x	500
664	P-aP?-P	31	P?	-	-	-	-	680-x	678-x
733	P	96	P	723	39	P	740	720	725
765	P-aP?-P	12	P?	785	2	aP	-	772-x	775-x
795	-	ϵ	-	804	3,5	aP	790	790	790
-	-	-	-	823	1,5	P?	-	-	825
921	P	7	P	-	-	-	-	908-x	917-x
955?	P?	ϵ	P?	952	18	P	-	965	-
-	-	-	-	975	ϵ	-	-	-	-
978	P-aP?-P	58	P	986	19	P	985	980	972
-	-	-	-	999	2	aP	-	990	995
1007?	aP?	ϵ	-	1015	ϵ	aP?	-	-	1025
1030?	-	ϵ	-	1035	1	aP?	-	1037	1040
1057	-	ϵ	-	1055	ϵ	-	-	-	-
-	-	-	-	1067	12,5	P	-	1065	1075
1109	-	ϵ	-	1113	ϵ	-	-	1087	1105
1120	P-aP	204	aP	1135	8,5	aP	1135	1129	1127
1160	P-aP	117	aP	-	-	-	-	1154	1148
-	-	-	-	1176	23,5	P	-	1190	1180-x
1205	-	ϵ	-	1193	3,5	aP	-	1205	1205
1222	P	63	P	1220	1	-	1225	1223	1222
1267	P-aP?-P	25	P?	1263	ϵ	-	-	1263	1270
-	-	-	-	1303	ϵ	-	-	1302	1308
1326	dP?-aP	276	aP	1316	46	aP	-	1325	-
-	-	-	-	1353	10	aP	1345	1342	1348
1365	P-aP-P	110	aP	1360	1	aP?	-	1365	1358
1390	?-aP	57	aP	1390	2	aP?	-	1409-x	1397-x
1457	-	ϵ	-	1453	ϵ	-	-	1442	1443
1481	P-aP?	36	aP	1492	15	aP	-	1497-x	1485
-	-	-	-	1509	2	aP	-	-	-
-	-	-	-	1530	2,5	aP	-	1538	1543
1550	P	40	P	1550	3,5	P	1550	1555	1555
1590	?-aP	34	aP	1580	3,5	aP	1585	1582	1587
-	-	-	-	1595	ϵ	-	-	-	-
1595	P	62	P	1605	30	P	-	1607	1615
1617	P	48	P	1615	ϵ	-	-	1620	1627
-	-	-	-	-	-	-	-	---	---

P : polarized, aP : anomalously polarized, dP : depolarized, ϵ : relative intensity < 1 . Relative intensities on F levels are I_F or I_{F_1} , according to the polarization state of the band under the same conditions of excitation.
-x : RR bands of pheophytin omitted, see ref. 7.

two molecules on irradiation of their F level (see below), and, in some cases, their relative intensities.

We have previously noted (1) that the RR spectra of porphin included all the frequencies observed in the fluorescence Shpolskii spectra. In table I we have compared the RR frequencies of mesoPdme with the vibrational frequencies obtained from the quasilinear fluorescence spectra of proto-porphyrin (6). Taking into account the chemical differences between the two molecules, the agreement appears satisfactory. As for porphin, the RR spectra contain more lines than the Shpolskii spectra ; it is not possible to decide at present whether this difference is simply due to technical factors, or if it has a theoretical basis. Besides, in table I, tentative correlations are also proposed with the RR frequencies of pheophytin a and b (7). Despite their chlorin structure and their fifth cycle, these molecules exhibit a high number of plausible correlations with RR frequencies of porphin and of mesoPdme in the $1100-1600\text{ cm}^{-1}$ region, where stretching motions of the tetrapyrrolic bonds are expected.

More interestingly, the RR frequencies cannot as a rule be correlated with the IR frequencies of mesoPdme, as was also found for D_{2h} porphin (8). This is shown in figure 3 for the $1000-1800\text{ cm}^{-1}$ region, and indicates that mesoPdme retains an effective symmetry which includes an inversion center, that is, D_{2h} , C_{2h} , or C_i . A similar mutual exclusion between IR and Raman activities was also observed for metalloporphyrins whose formal symmetry excludes an inversion center, but which possess an apparently unperturbed double bond system (9).

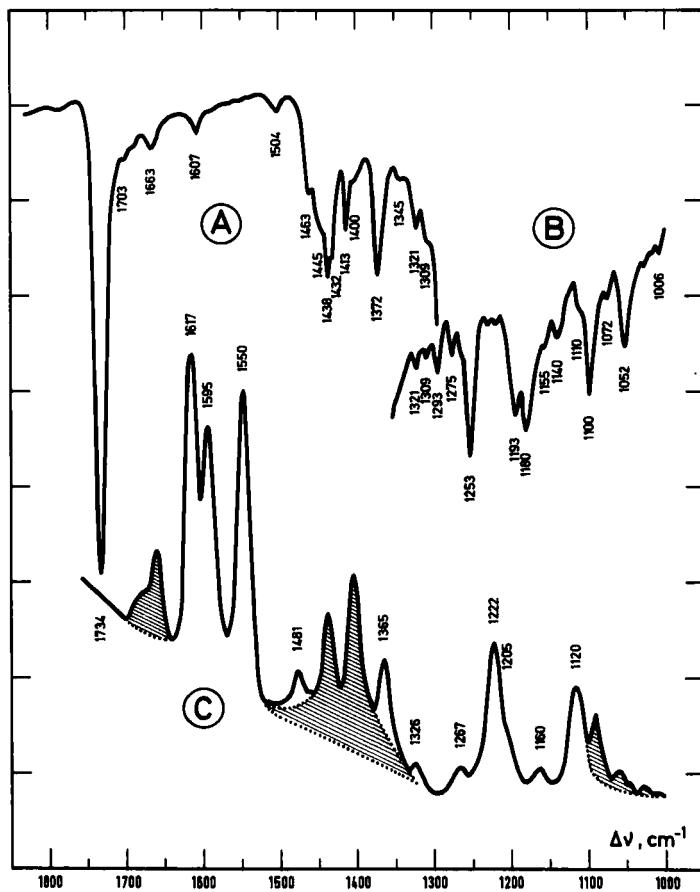


Figure 3 : Partial IR spectra of mesoPdme, A : in Voltalef,
 B : in Nujol. C : RR spectrum (I_{\parallel}) of MesoPdme in
 DMF ; $\lambda_{\text{exc}} = 465.8$ nm. DMF bands are shaded.

Variations of depolarization ratios

We have calculated where possible the depolarization ratios of fourteen bands of mesoPdme for each of the ten irra-

diation wavelengths. Typical plots of these ratios against irradiation wavelength are reproduced in figures 4 and 5.

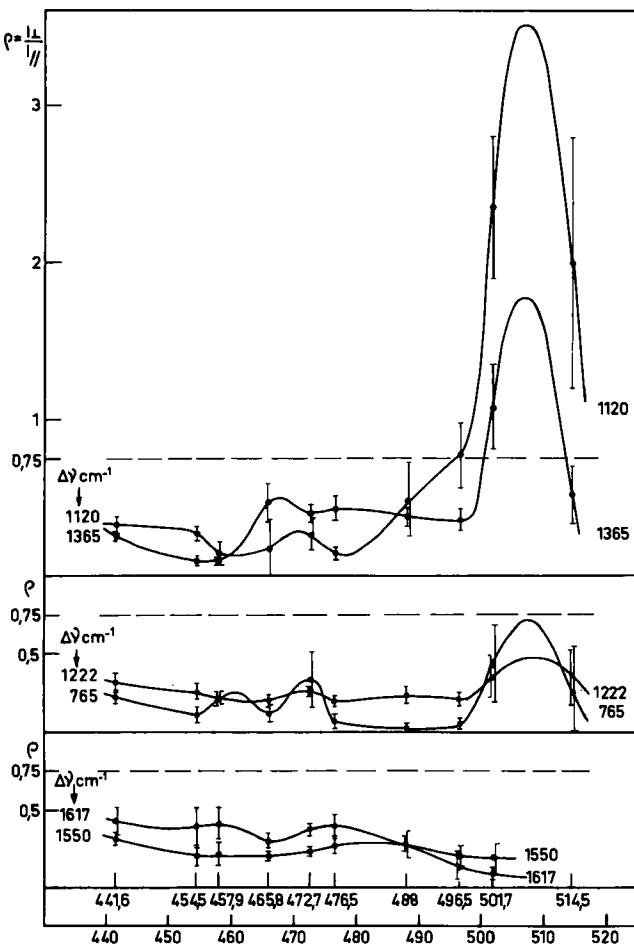


Figure 4 : Variations of depolarization ratios with excitation wavelength. From top to bottom : classes b), d) and a).

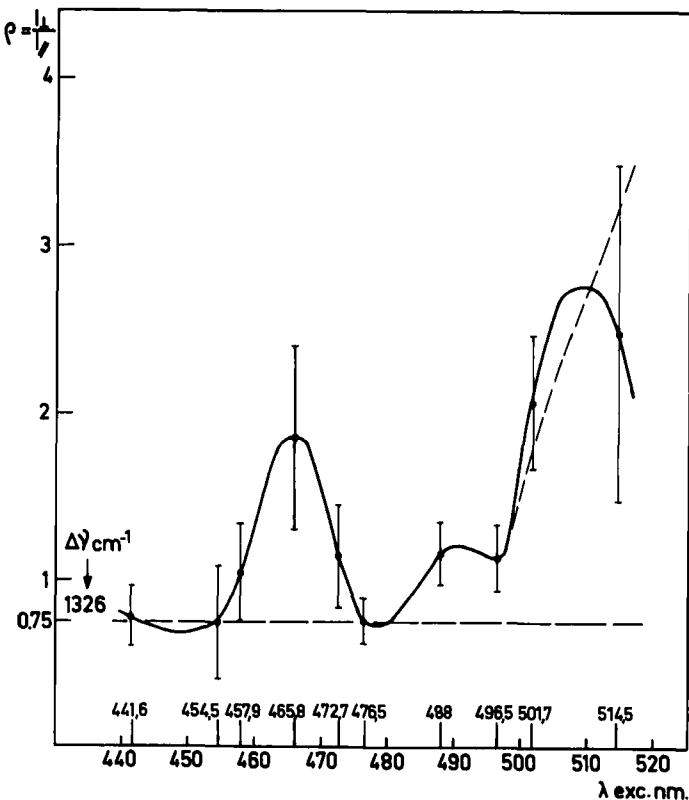


Figure 5 : Variations of depolarization ratios with excitation wavelength - class c).

We tentatively distinguish 4 types of variation of $\rho(\lambda_{\text{exc}})$:

- Bands polarized throughout the excitation range and having no maximum around 505 nm : 1550 and 1617 cm^{-1} (fig. 4).
- Bands having one maximum of anomalous polarization ($\rho > \frac{3}{4}$) in the 505 nm range, that is, close to the F level (see below), and polarized in the remaining spectral regions : 1120 , 1160 and 1365 cm^{-1} (fig. 4).

c) Bands anomalously polarized throughout the excitation range : 1326 cm^{-1} (fig. 5). Also, the 1390 and 1590 cm^{-1} bands, with very low I_{\parallel} intensities, most probably belong to this type.

d) Polarized bands having a maximum in ρ at about 505 nm , which probably remains under 0.75 : $240, 664, 733, 765, 978, 1222, 1267$ and 1481 cm^{-1} (fig. 4). Some of these bands, particularly the last one, may actually belong to types a) or b).

Four other bands, at $322, 480, 921$ and 1595 cm^{-1} , which have very low I_{\perp} intensities can most probably be included in one of the 3 groups a), b), or d).

This classification divides RR vibrations of mesoPdme into four categories with respect to their symmetry properties. Even if one assumes that all the bands of class d) can be included in categories a) and/or b), the existence of at least three distinct categories strongly suggests that mesoPdme retains an effective D_{2h} symmetry (four Raman active symmetry types) rather than a C_{2h} or C_1 symmetry (two and one Raman active types, respectively).

Limits may be set for the variations of ρ for a vibration of a given symmetry type belonging to a given point group by making use of the elementary scattering tensors tabulated by McClain (10). For the D_{2h} point group, totally symmetric vibrations (A_g) should remain polarized, while non totally symmetric Raman active vibrations (B_{1g}) should have $\rho \geq \frac{3}{4}$. Classes a), c) and d) defined above respectively fill these requirements for mesoPdme. However, as in the case of porphin, bands of class b) behave in a way which is contradictory with an effective D_{2h} symmetry for mesoPdme in its ground and lower

excited states (1). We leave this question open for the present, inasmuch as the following discussion does not invoke the effective symmetry of mesoPdme.

Variations of band intensities.

Variations of I_{\parallel} and I_{\perp} with illuminating wavelength were followed for fourteen of the twenty three RR bands observed for mesoPdme. For six other bands, only I_{\parallel} or I_{\perp} variations could be studied, the other component being too weak to be measured with any accuracy. The three remaining frequencies 795, 1205 and 1457 cm^{-1} , corresponded to shoulders, or bands with very weak I_{\parallel} and I_{\perp} intensities. Figure 6 shows the complete series of spectra in the 1280-1480 cm^{-1} region. Figure 7 shows representative excitation profiles for three of the bands studied, on a logarithmic intensity scale.

For most of the 34 profiles, 3 maxima in intensity are observed at about 505 ± 2 , 470 ± 2 and 459 ± 4 nm (fig. 7, 8). Using the notation employed previously for porphin (2), these will be referred to hereafter as the F, L and S maxima.

The F maxima are generally very strong and the L maxima are also easily observed, whereas the S maxima are weaker and hence less precisely located ; as in the case of porphin, these last appear clearly for only a half of the bands studied.

Some excitation profiles exhibit one or two supplementary maxima, e.g. the I_{\parallel} profile of band 765 cm^{-1} (Fig. 7), and these maxima appear to have a variable position depending on the band studied (Fig. 8).

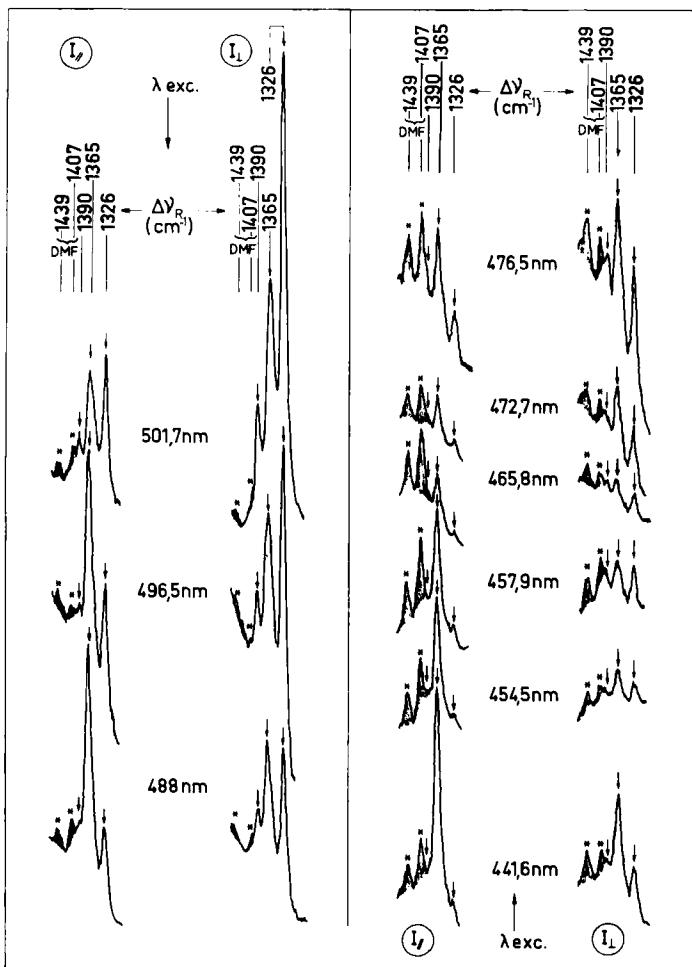


Figure 6 : Partial RR spectra of mesoPdme in DMF (1300 to 1450 cm^{-1}), 441,6 to 501,7 nm excitation.

* : DMF bands.

Finally, most of the bands increase smoothly in intensity below 455 nm, most probably on account of preresonance in the

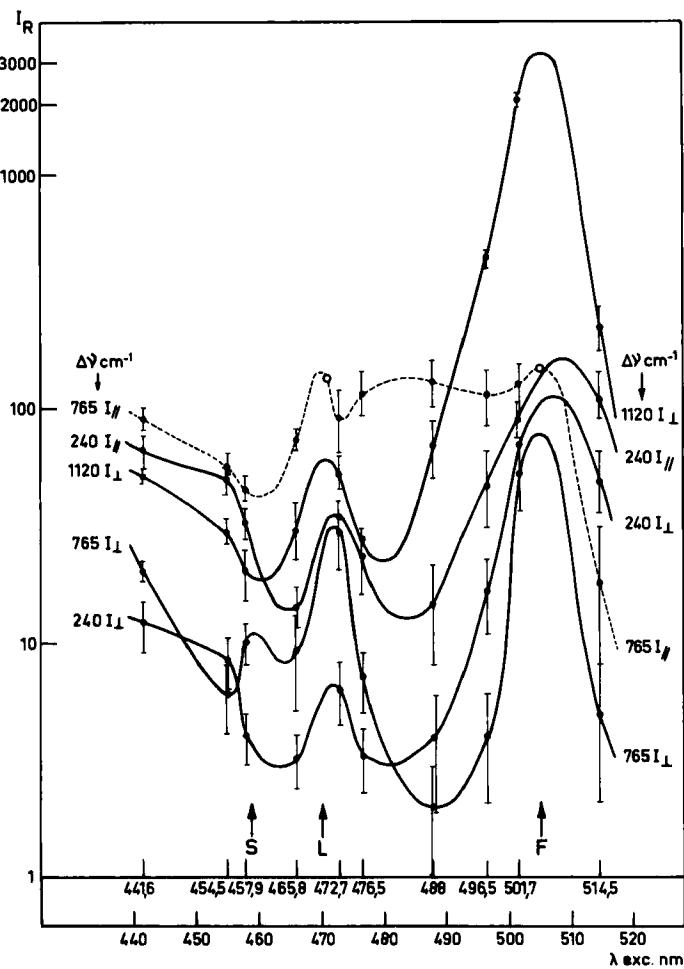


Figure 7 : Excitation spectra for the 240 , 765 and 1120 cm^{-1} bands of mesoPdme in DMF. Relative intensities, corrected for instrumental sensitivity and reabsorption. Black circles : experimental values. White circles : values calculated from $I_{//} = \frac{I_{\perp}}{\rho}$.

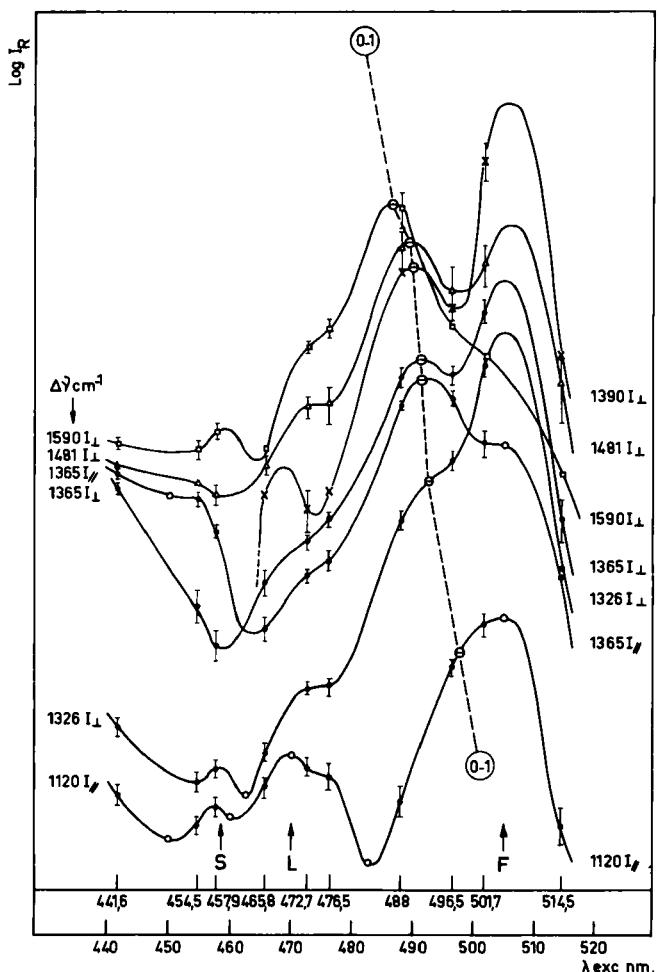


Figure 8 : Excitation spectra for 6 RR bands of mesoPdme in DMF. Corrected intensities. Individual ordinate scales are translated in order to show the displacement of the secondary maxima III (0-1) with the frequencies of the bands under consideration.

Soret band system (Fig. 1). Figure 9 depicts the positions of all the observed intensity maxima (upper section), in relation to the observed electronic spectrum of mesoPdme (lower section).

F, L and S maxima : These three maxima occur at the same wavelengths, regardless of the frequency of the Raman band under consideration. Previous observations (11) and theoretical predictions (12) have indicated that a given Raman frequency $\Delta\nu_R$ may exhibit a resonance maximum when excited at the frequency ν_0 of a purely electronic, allowed transition, and also at the frequency $\nu_0 + \Delta\nu_R$ of the corresponding vibrational sublevel of that transition. As in the case of porphin (2), the F, L and S maxima are thus likely to correspond to purely electronic transitions present in band IV of mesoPdme. This hypothesis is in contradiction with the current interpretation of the electronic spectra of porphyrins, which assigns band IV to vibrational sublevels of band III (13, 14). For mesoPdme, as for porphin, the F and L levels correspond to features of band IV observable at room temperature. However, level S has no apparent correspondence in these conditions.

Table II compares the energy differences measured between the F, L, S and III transitions of each of the two molecules. The separations F-III and S-L are similar for both, while that of the F and L levels is greater for mesoPdme than for porphin. This explains why the other types of intensity maxima were more clearly observed for mesoPdme.

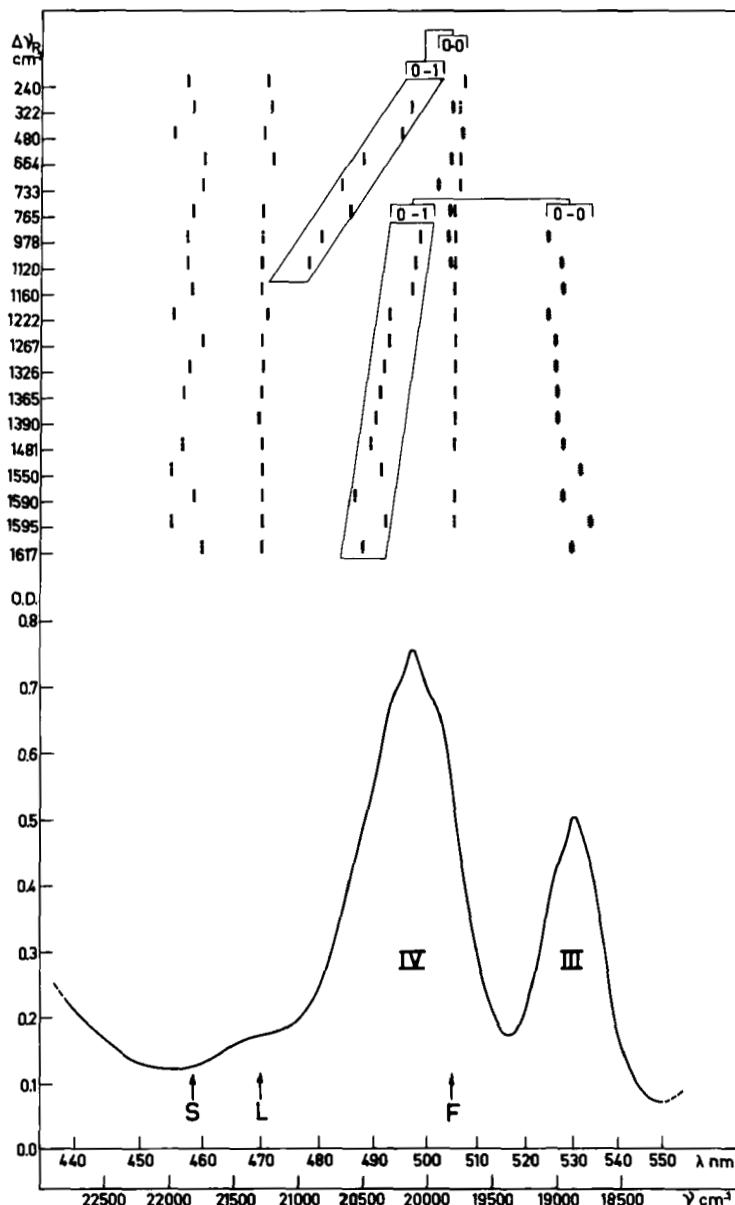


Figure 9: Positions of maxima and shoulders of the excitation spectra of RR bands of mesoPdme in DMF, relatively to the absorption spectrum. See text.

TABLE II

Energy differences between the F, L, S and III electronic levels in porphin and mesoporphyrin dimethylester.

$\Delta E, \text{ cm}^{-1}$	S-L	L-F	F-III*
MesoPdme	510	1470	950
Porphin	545	645	1100

* Position of level III was identified with the top of band III : mesoPdme : $18\ 850 \text{ cm}^{-1}$, Porphin : $19\ 300 \text{ cm}^{-1}$.

Other maxima : Figure 8 suggests that the higher the frequency of the RR band under consideration, the shorter the wavelength at which these secondary maxima appear. We subtracted the Raman frequency from the absolute frequency of each of these maxima and plotted the corresponding wavelengths on figure 9 (crosses). It is seen from this figure that these wavelengths fall into two clearly defined spectral regions, one near the maximum of band III, and one near the F level at 505 nm. Following the conclusions of the studies cited in the preceding section, these maxima may be interpreted as resonances on vibrational sublevels of band III, and of level F. In our opinion, this point strongly confirms the hypothesis that level F actually corresponds to a pure electronic transition.

The overlapping of maxima and discrete excitation wavelengths explain why neither the resonances on vibrational

sublevels of band III for $\Delta\nu_R \leq 765 \text{ cm}^{-1}$ nor those of transition F for $\Delta\nu_R \geq 1160 \text{ cm}^{-1}$ are observed.

Very recent theoretical work (15) has indicated that resonance of a Raman band at both excitation frequencies ν_0 and $\nu_0 + \Delta\nu_R$ is restricted to the case of non totally symmetric vibrations coupled to both ground and resonating (ν_0) electronic states, while resonance(s) of totally symmetric modes need not coincide with either of these two levels. This theory should apply to mesoPdme, and should lead to the same interpretation, in so far as some experimental evidence (16) indicates that vibrational structure of ground and lower excited electronic states of the various porphyrins should not be very different, and also, as we showed above, that whatever the effective symmetry of mesoPdme (D_{2h} , C_{2h} or C_1), non totally symmetric modes are active in the present RR spectra. However, the present results indicate that totally symmetric vibrations (e.g. 1550 and 1617 cm^{-1}) actually resonate at levels F, L and S, as well as at vibrational sublevels of band III (fig. 9).

CONCLUSION

By revealing the presence of five different types of resonance enhancing levels in band IV of mesoPdme, the present results support our previous hypothesis (2) that band IV of metal free porphyrins is more complex than it has been generally suspected ; this band probably includes not only vibrational sublevels of band III, but also three purely electronic

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transitions, and vibrational sublevels of at least one of these (F). As far as mesoPdme is concerned, new vibrational data are reported ; and the new excitation profiles obtained for depolarization ratios, although not yet fully interpreted, suggest that mesoPdme in solution which probably retains an inversion center, may assume an effective D_{2h} symmetry.

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