A Spectral Study of Matrix-Isolated Porphine, Zinc Porphine, and Copper Porphine

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Abstract: Porphine was studied in Ar, SF_6, and *n*-octane matrices. A complex visible absorption spectrum and the expected split Soret transition were observed. Zinc and copper porphine were also studied in these matrices and in an NH_3 matrix; both exhibited unusual quasiline spectra in the visible and Soret region. The spectra are explained by assuming the molecules are trapped as pairs or "dimers" in the matrix.

Several absorption and emission spectral studies of porphyrins and phthalocyanines isolated in a matrix or frozen solution have been reported.[2-6] Antenson and Hocstrasser[2] observed "quasilines" or Shpolskii lines[7] in the absorption spectrum of porphine in frozen octane solution. The Russian workers have reported quasiline spectra (absorbance and fluorescence) for several porphyrins in frozen solutions at 77°K.[3] They interpret their observations in terms of the molecular vibrations of the porphyrins which are active in the electronic spectrum and the different orientations of the porphyrin molecule with respect to the crystal axis of the frozen host. Meyer, *et al.*,[4] reported quasiline absorption and emission spectra for free base and metal phthalocyanines isolated in argon matrices.

Lucia, Verderame, and Taddei[6] studied the absorption spectrum of argon-matrix-isolated free base and copper phthalocyanines and found no quasilines. They found that the free base absorption spectrum resembled the solution spectrum; however, for the copper complex, they found a band on the red side of the expected 6800-Å band and its intensity varied directly with the concentration of the copper phthalocyanine in the sample. They assumed this effect to be due to guest–guest pair interactions in the matrix. By using known atom–atom pair potential functions, they calculated the most stable geometry for a pair of phthalocyanine molecules as a function of the distance between centers, *r*. The Davydov splitting[8] for each stable configuration was calculated as a function of *r*. A stable configuration was found whose resulting Davydov splitting agreed well with that observed experimentally. Again, this effect was observed only with the copper complex and not with the free base.

In this study, porphine and zinc and copper porphine were studied in *n*-octane, argon, and sulfur hexafluoride matrices; ZnP was also studied in an ammonia matrix. In some of the frozen solution spectral studies, it appears that traces of benzene were added to the hydrocarbon solvent to dissolve the porphyrin.[3] Isolating the compounds in the hydrocarbon matrix avoided any complications that added benzene may introduce and resulted in more homogeneous samples than the frozen solution technique.

Experimental Section

The porphine used in this study was prepared by the acid-catalyzed condensation of pyrrole-2-carbinol in 10% acetic acid–xylene solution.[9] The zinc and copper porphines were prepared by the method of Adler, *et al.*[10] Spectral quality *n*-octane was stored over metallic sodium and distilled prior to use. Ultrapure argon and sulfur hexafluoride obtained from Matheson Co. were used as supplied.

The Knudsen deposition technique employed in this study was similar to the method of Meyer, *et al.*,[4] and of Lucia, *et al.*[6] The Knudsen oven was attached to an Air Products Cryo-Tip (heat exchanger Model AC-2-110 and vacuum shroud WMX-1A). Iron–constantan thermocouples were positioned at the window holder and in the Knudsen oven so that the temperatures of the emitted vapor could be measured. (The Cryo-Tip was evacuated to a pressure of about 10^{-5} Torr.)

The spectra were recorded in a single beam mode with a Gilford Model 240 spectrophotometer modified as follows. A 1.0-rpm synchronous motor was used to rotate the wavelength drive shaft, and the output from the instrument's photomultiplier amplifier circuit, which is logarithmic in intensity, was led to a Leeds and Northrup Speedomax WL strip chart recorder. In this manner, the instrument could scan and record spectra. In each experiment, a recording was made through a blank matrix to establish a base line. The matrix-isolated sample was then prepared by the usual codeposition technique and the spectrum recorded. The base line was subtracted point by point to yield a corrected spectrum. The Gilford monochromator was calibrated with a low-pressure mercury lamp. The spectral band width was 0.70 nm at 600 nm and 0.20 nm at 400 nm.

From the pressure change in the vacuum manifold used to manipulate the host gas, the number of moles of host deposited could be calculated. After each experiment, the host gas was allowed to evaporate leaving a film of the deposited porphyrin on the target window and holder. This was washed off with benzene, the absorption spectrum of the solution was recorded on a Cary 14 recording spectrophotometer, and thus, from the molar extinction coefficients, the number of moles of deposited porphyrin was estimated. This method also provides a check on the purity of the guest in each experiment.

The fluorescence emission and excitation spectra of zinc porphine was obtained with the Aminco-Bowman spectrophotofluorimeter using a Hammamatsu R 446 photomultiplier (S-20 spectral response).

Results

Porphine. The room-temperature solution spectra of

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[1] NIH predoctoral fellow, 1970–1972, GM-48947.

[2] J. Antenson, Ph.D. Dissertation, University of Pennsylvania, 1971.

[3] G. P. Gurinovich, A. N. Sevechnko, and K. N. Solev'ev, "Spectroscopy of Chlorophyll and Related Compounds," Izdatel'stvo Nauka i Teknika, Minsk, 1968. Translated by the U. S. Joint Publications Research Service, Washington, D. C.

[4] E. Bajema, M. Gouterman, and B. Meyer, *J. Mol. Spectrosc.*, 27, 225 (1968).

[5] K. E. Rieckhoff and E. M. Voigt, "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 295.

[6] E. A. Lucia, F. D. Verderame, and G. Taddei, *J. Chem. Phys.*, 52, 2307 (1970).

[7] E. V. Shpolskii, *Dokl. Akad. Nauk SSSR*, 87, 935 (1952).

[8] A. S. Davydov, *J. Exp. Theor. Phys.*, 18, 210 (1948).

[9] S. Beitchman, Ph.D. Dissertation, University of Pennsylvania, 1968.

[10] A. D. Adler, F. R. Longo, F. Kampus, and J. B. Kim, *J. Inorg. Nucl. Chem.*, 32, 2443 (1970).

Table I. Matrix-Isolated Porphine[a]

Solution[b], [19] λ, Å	Octane 23 °K λ, Å	$\Delta\lambda_{1/2}$, Å	Argon 23 °K λ, Å	$\Delta\lambda_{1/2}$, Å	SF$_6$ 23 K° λ, Å	$\Delta\lambda_{1/2}$, Å
6173	6104	(40)	6085	(30)	6090	(35)
6070 shd	6050	(Shd)	6020	(Shd)	6035	(20)
5900 shd	5980	(20)	5955	(Shd)	5970	(Shd)
5830 shd	5872	(25)	5850	(10)	5930	(Shd)
	5800	(10)	5780		5865	(15)
	5715	(Shd)	5700	(Shd)	5790	(Shd)
					5710	(Shd)
5710	5662	(40)	5635	(25)	5650	(30)
5640	5588	(35)	5565	(30)	5580	(35)
5550 shd	5500	(10)	5525	(Shd)	5540	(Shd)
5410 shd	5394	(20)	5470	(Shd)	5495	(Shd)
			5440	(20)	5460	(Shd)
					5370	(Shd)
5208	5162	(32)	5140	(Shd)	5140	(Shd)
	5138	(Shd)	5108	(15)	5110	(20)
4902	4900	(Shd)	4890	(Shd)	4905	(Shd)
4830 shd	4880	(20)	4850	(20)	4855	(50)
4720 shd	4830	(Shd)	4810	(20)	4810	(Shd)
4645 shd	4816	(Shd)	4755	(Shd)	4765	(Shd)
	4708	(Shd)	4738	(15)	4675	(20)
	4694	(Shd)	4670	(Shd)		
3965	3940	(50)	3890	(Shd)		
	3860	(40)	3840	(80)		

[a] The four visible bands and the Soret band regions are grouped together; shd = shoulder. [b] Those peaks not marked shd are the predominant peaks in the solution spectrum.

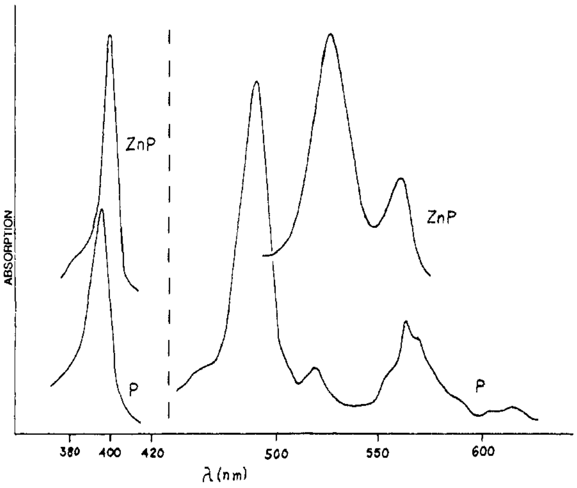

Figure 1. Benzene solution spectra of porphine[1] and ZnP[2] at room temperature.

Table II. Matrix-Isolated ZnP (23 °K)

Band	Solution λ, Å	$\Delta\lambda_{1/2}$, Å	Octane λ, Å	$\Delta\lambda_{1/2}$, Å	Argon λ, Å	$\Delta\lambda_{1/2}$, Å	SF$_6$ λ, Å	$\Delta\lambda_{1/2}$, Å	NH$_3$ λ, Å	$\Delta\lambda_{1/2}$, Å
			d 3830							
Soret	3990	(110)	c 3890	(Shd)	3740	(Shd)	d′ 3600		3850	
			b 3940	(50)	d 3795	(10)	c′ 3620		4070	(45)
			a 4050	(Shd)	c 3850	(30)	b′ 3645	(10)		
					b 3900	(10)	a′ 3685	(10)		
					a 3925	(10)	d 3730			
							c 3785	(10)		
							b 3840	(30)		
							a 3880	(10)		
Q(1–0)	5255	(215)	5130	(15)	5110	(Shd)	5090	(25)	5290	(Shd)
			5220		5180	(40)	5155	(20)	5370	(100)
			5200		5230	(15)	5220	(Shd)	5490	(Shd)
			5270	(20)	5300	(Shd)	5290	(Shd)		
			5330	(Shd)						
Q(00)	5590	(120)	d 5440	(15)	5420		5405	(10)	5720	(80)
			c 5490	(15)	5472	(10)	5460	(15)		
			b 5532	(30)	5514	(30)	5500	(20)		
			a 5620	(30)	5570	(20)	5570			

porphine and ZnP are shown in Figure 1. The porphine spectrum contains many peaks and shoulders and is more complicated than those of its substituted derivatives. The matrix spectra of porphine (Figure 2) show many features but most of these are present in the solution spectrum and are only sharpened at the lower temperature. The matrix spectra are very similar to the frozen ethanol solution spectrum reported by Rimington, *et al.*[11] The peak position and relative intensities were independent of mole ratio and deposition temperature in all matrices. The expected matrix spectral shifts were observed.

The number of features in the visible spectrum decreases along the matrix series octane, SF$_6$, Ar (see Table I). Annealing of the SF$_6$ and octane of matrix-isolated samples caused no spectral changes. The splitting of the Soret transitions predicted by theory[12] was observed in the argon- and octane-matrix spectra. The Soret was not recorded for the SF$_6$-isolated sample.

Zinc and Copper Porphine. As Figure 1 shows, the solution spectrum of ZnP is much simpler than that of the free base. There are two distinct visible bands not complicated by shoulders and a sharp single Soret band. The matrix spectra of ZnP and CuP (Figures 3 and 4) are much more complex. There are many peaks or quasilines in the visible and Soret regions. The peak positions and relative intensities listed in Tables II and III were independent of mole ratio and deposition temperature in all cases. Except for the NH$_3$-matrix-isolated sample, there are four quasilines for Q(0–0) and at least four quasilines in the Soret region. If one labels the four quasilines in a set as a, b, c, and d in order of increasing energy, then for the Q(0–0) transition of ZnP in all matrices except NH$_3$ and the first four features in the Soret region of ZnP and CuP in SF$_6$ and octane, the relative intensities are $b > c > d \simeq a$. Annealing caused no change in the number of features

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(11) H. Rimington, S. F. Mason, and O. Kennard, *Spectrochim. Acta*, **12**, 65 (1958).

(12) M. Gouterman, *J. Mol. Spectrosc.*, **6**, 138 (1961).

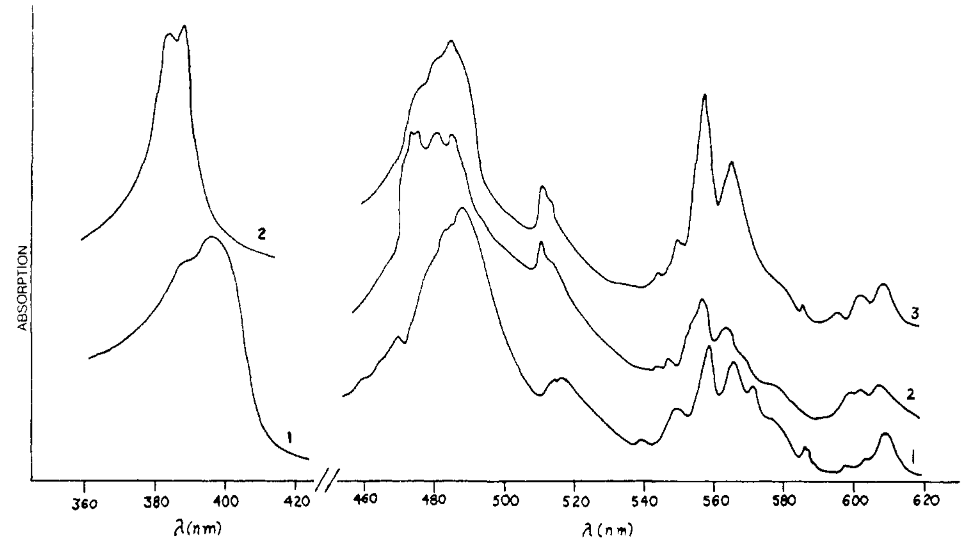

Figure 2. Visible absorption spectra of matrix-isolated porphine at 23°K: (1) *n*-octane matrix, 3500:1 mol ratio; (2) Ar matrix, 4000:1 mol ratio; (3) SF_6 matrix, 3500:1 mol ratio.

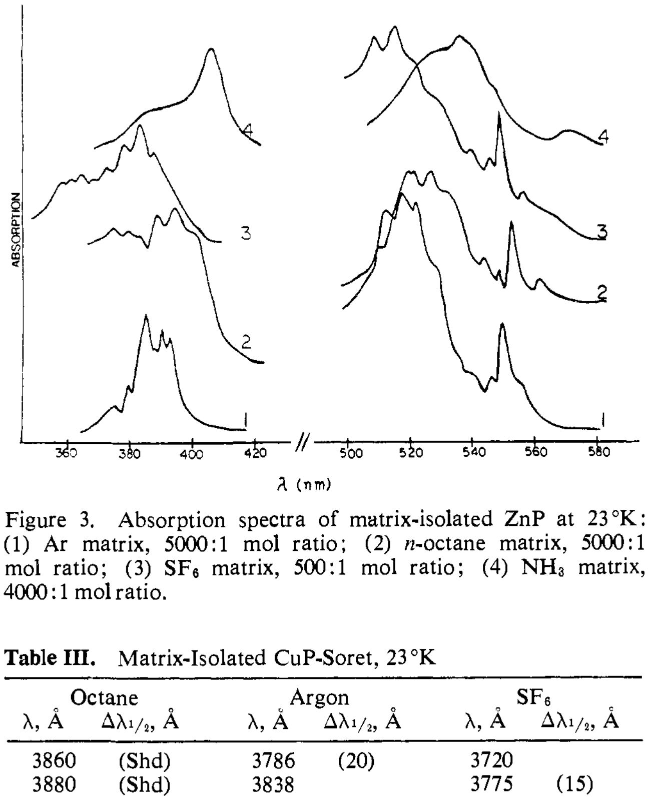

Figure 3. Absorption spectra of matrix-isolated ZnP at 23°K: (1) Ar matrix, 5000:1 mol ratio; (2) *n*-octane matrix, 5000:1 mol ratio; (3) SF_6 matrix, 500:1 mol ratio; (4) NH_3 matrix, 4000:1 mol ratio.

Table III. Matrix-Isolated CuP-Soret, 23°K

Octane		Argon		SF_6	
λ, Å	$\Delta\lambda_{1/2}$, Å	λ, Å	$\Delta\lambda_{1/2}$, Å	λ, Å	$\Delta\lambda_{1/2}$, Å
3860	(Shd)	3786	(20)	3720	
3880	(Shd)	3838		3775	(15)
3910	(Shd)	3850		3835	(25)
3940	(25)	3870		3900	(60)
4020	(60)	3908	(10)	3980	(Shd)
4080	(20)	3925	(Shd)		
		3960	(10)		
		3994	(10)		

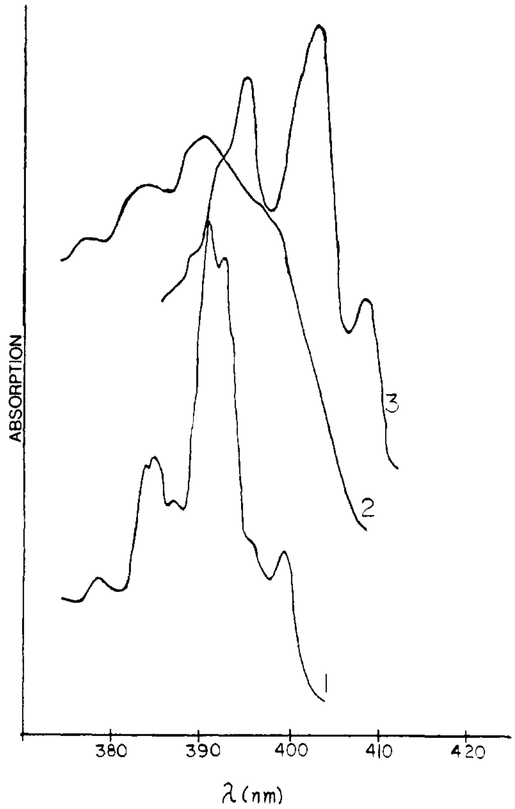

Figure 4. Soret region absorption spectra of matrix-isolated CuP at 23°K: (1) Ar matrix, 4000:1 mol ratio; (2) SF_6 matrix, 3500:1 mol ratio; (3) *n*-octane matrix, 2500:1 mol ratio.

or their relative intensities. The Soret region spectra of both ZnP and CuP are somewhat more complicated.

A 23°K spectrum of a ZnP film deposited on the target showed two bands with no quasiline structure in the Q(0–0) region; the two bands almost merge at 77°K.

A saturated *n*-octane solution of ZnP was prepared without addition of benzene and the Soret region fluorescence excitation and emission spectra were recorded (Figure 5) at room temperature and at 77°K. At 77°K there appears to be a shoulder to the red of the expected Soret in the excitation spectrum. In the emission spectrum, the Q(0–0) band was not split at 77°K but Q(1–0) did split into three features. The spectra were quite distorted due to scattering from the snow.

Discussion

Porphine. Many of the features present in the porphine-matrix spectra are also present in the benzene solution spectrum and in the frozen ethanol solution spectrum.[11] Since annealing caused no spectral changes for the SF_6- and *n*-octane-matrix-isolated samples, and the spectra were independent of mole ratio, we feel that the observed features or quasilines result from the resolution of vibronic transitions rather than from some peculiar guest–host interaction or different site symmetries in the host. Also, any guest–host interactions would be expected to affect the Soret region but no effect was observed there.

Metal Porphines. The interesting effect observed for ZnP and CuP, namely, the appearance of four quasilines in the Q(0–0) region and at least four in the Soret region, is probably not due to some guest–host interaction. It is observed in three different hosts, Ar, *n*-octane, and SF_6. It is absent only with the NH_3 host. Also, the effect does not occur with free base porphine; one could argue that it would be masked by the many peaks in the visible spectrum of free base porphine, but it is clearly absent in the Soret region. One would not expect such a difference between the porphine and metalloporphine spectra if guest–host interactions were at work. A host molecule just should not "see" much difference between CuP or ZnP and porphine. All have the same basic geometry.

The effect is probably not vibronic since there is only one simple band at 5720 Å in the Q(0–0) region of the NH_3 matrix spectrum (with a half-width less than the splitting in the other matrices) and two bands in the Soret region at 4070 and 4038 Å with an energy spacing of 1400 cm^{-1}. No doubt, these are B(0–0) and B(1–0). Two peaks at approximately the same wavelength were observed in the fluorescence excitation spectrum in *n*-octane. The three peaks in the Q(1–0) region of the NH_3 matrix spectrum (Figure 3) at 5290, 5370, and 5490 Å are probably three vibronics which overlap to give the observed Q(1–0) in solution. This is supported by the observed splitting of Q(0–1) into three peaks in the fluorescence spectrum at 77°K of a frozen octane solution of ZnP.

The effect is also not due to isolation of ZnP crystallites, since it was not observed in the ZnP film spectrum. The ZnP thin film spectrum shows two broad peaks in the Q(0–0) region at 23°K and these have merged into one at 77°K.

The effect may be due to pairing of the metal porphine molecules to form "dimers." The formation of a dimer of low symmetry would remove the double degeneracy of the molecular excited states, and each molecular state would undergo Davydov splitting[8] to give two transitions for a total of four. This would account for the appearance of four quasilines in the Q(0–0) region and at least four in the Soret region for the Ar, *n*-octane, and SF_6 matrix spectra. Since NH_3 is a strong ligand, it could work to reduce the intermolecular interactions required for dimer formation and no quasilines would be observed in this matrix. Also, the B(1–0) vibronic observed in the NH_3 matrix absorption spectrum and in the frozen *n*-octane excitation spectrum would also be split by pair formation in the other matrices and this would account for the additional features in the Soret region. The three Q(1–0) vibronics which were observed in the NH_3 matrix would each be split accounting for the complex pattern observed in the Q(1–0) region of the Ar, *n*-octane, and SF_6 matrix spectra. The appearance of some doublet peaks in the Soret region of the Ar matrix spectra and the deviation from the intensity pattern observed in the other matrices could indicate two slightly different dimer sites in the Ar matrix or two slightly different dimer configurations.

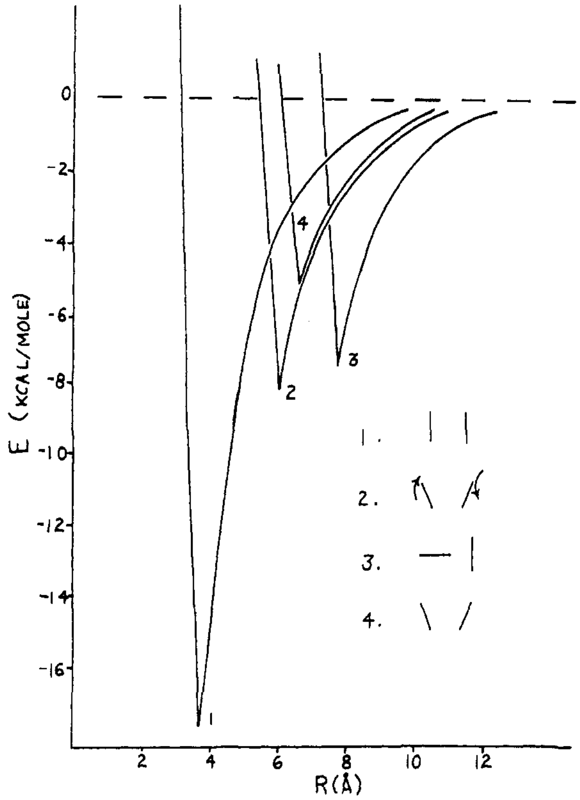

Figure 5. Potential curves: (1) parallel sandwich, 45° rotation; (2) 45° sandwich, 45° rotation; (3) end on, 45° rotation; (4) 45° sandwich, 0° rotation. Sketches indicate relative orientation of porphine planes.

Lucia, Verderame, and Taddei[6] used the concept of pair formation and resultant Davydov splitting to explain their results with argon-matrix-isolated copper phthalocyanine. They did not observe this effect for the free base. In this study, we also observed an effect only for the metal porphine, but we observe no concentration dependence. Our results suggest that if we are seeing guest pairing, the metal porphine is either completely dimerized in the vapor, and it is these dimers which are isolated in the matrix, or by some mode of action the metal porphine molecules become completely paired in the matrix. Increasing the deposition temperature to 350° (a 70° increase) has no effect on the spectrum. We feel that such a temperature increase would certainly affect the state of aggregation in the vapor and, therefore, we must conclude that pairing is occurring after or during deposition. Unfortunately, Gouterman and Edwards[13] did not study any metal porphines in their extensive vapor phase spectral study of porphyrins. A mass spectral search for dimers in ZnP vapor gave inconclusive results.

The pair model gives quantitative results which are in fair agreement with experiment. The observed energy spacings are listed in Table IV. To calculate the Davydov splittings, the orientation of the two molecules in the proposed pair must be known. Unfortunately, the crystal structures of zinc and copper por-

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[13] L. E. Edwards, Ph.D. Dissertation, Harvard University, 1969.

Table IV. Experimental Splittings (cm^{-1}), 23 °K

Compound	Band	Octane			Argon			SF_6		
ZnP	B(1–0)							d′	27,778	
										154
								c′	27,624	
										189
								b′	27,435	
										298
					a′	26,738*		a′	27,137	
							388			327
	B(0–0)	d	26,110					d	26,810	
				405	a	26,350				
		c	27,507							390
				327			376	c	26,420	
										378
		b	25,380		c	25,974		b	26,042	
				690			334			269
		a	24,690		b	25,640		a	25,773	
							163			
					a	25,477				
	Q(0–0)	d	18,382		d	18,450		d	18,500	
				167			175			185
		c	18,215		c	18,275		c	18,315	
				138			142			133
		b	18,077		b	18,133		b	18,182	
				283			180			229
		a	17,794		a	17,953		a	17,953	
CuP	B(10)	b′	25,907			26,413		a′	26,882	
				134			358			392
		a′	25,773			26,055		d	26,490	
				198			80			425
	B(00)	d	25,575			25,975		c	26,075	
				195			135			434
		c	25,380			25,840		b	25,641	
				505			260			516
		b	24,875			25,580		a	25,125	
				365			103			
		a	24,510			25,477				
							224			
						25,253				
							116			
						25,037				

phine have not yet been determined. Porphine[14] has been studied, but assuming that its metal derivatives have the same crystal structure is poor in light of the situation with *meso*-tetraphenylporphine and its metal derivatives.[15] Porphine is monoclinic with four molecules per unit cell. The distance between planes of neighboring molecules is 3.42 Å. The dipole–dipole approximation should be applicable to the Soret transition since it is so intense; it should not be applicable to Q(0–0), since this is a weak transition. Davydov splitting for two metal porphine molecules oriented as in the free base porphine crystal with the above distance is ±4000 cm^{-1}, much larger than is observed, and only two transitions would be expected in the Soret region.

Following Lucia, *et al.*,[6] we performed a pair potential calculation by computer to determine stable configurations of a dimer. For a given configuration, the total energy was calculated as a sum of pair potential energies, the sum being taken over all pairs of atoms. Each configuration of the two metal porphine molecules requires 1296 such pair interactions. For the H–C, C–C, and H–H interactions, the potential function $V_{ij} = A \exp(-Br_{ij}) - C/r_{ij}^6$ was used. The constants A, B, and C were those reported by Williams for aromatic compounds.[16] For the N–N, N–H, and C–N interactions, the Lennard-Jones potential function with constants proposed by Scheraga, *et al.*,[17] was used. The results are shown in Figure 5. The first and lowest energy minimum occurs at 3.5 Å between centers with the two molecular planes parallel. This is referred to as the "parallel sandwich structure." From 5.5 to 7.25 Å between centers, several stable structures occur. The most stable one occurs at 5.75 Å with a 45° dihedral angle between molecular planes and the plane of one molecule twisted 45° relative to the other. This twist appears to lower the energy by about 2.5 kcal/mol relative to the untwisted configuration. This twisted configuration will be referred to as the "45° sandwich structure." At a distance of 7 Å, the most stable configuration appears to be one with the plane of one molecule normal to that of the other. Twisting the vertical molecule by 45° about the vertical axis seems to have little effect on the energy. This structure will be referred to as the "end on structure."

The parallel sandwich structure is very similar to the relative orientation of two porphine molecules in the free base crystal. This arrangement is of D_{4h} symmetry or D_{4d} if the planes are twisted. In either case, the E_u free molecule states will correlate with some E species of the dimer point group. Thus, two degenerate dimer states are predicted. The end on structure is of C_{2v} symmetry and the E_u molecular state correlates with B_1, B_2, and A_1, B_2. A_1 is forbidden; thus, three transitions are predicted.

In the 45° sandwich structure, which is approximately of C_{2v} symmetry, the E_u molecular states are split into two states which for simplicity will be referred to as X and Y ($X = A_2 + B_1$; $Y = A_1 + B_2$). Each state undergoes Davydov splitting with the corresponding state of the neighbor molecule in the pair, thus giving four transitions. The X and Y splittings for ZnP were calculated (see Appendix) to be ±720 and ±510 cm^{-1}, respectively. In CuP, they were calculated to be ±1130 and ±795 cm^{-1}, respectively. These splittings are in fair agreement with those observed if one assigns bands a and d as those resulting from the X states and b and c from the Y states.

Since metalloporphyrins are known to bind one or two ligands in the axial positions, one may try to explain the appearance of additional features in the matrix absorption spectrum by postulating that the zinc or copper porphine is complexed with some ligand, thus lowering the symmetry from D_{4h} and lifting the double degeneracy of the metal porphine excited states. One can also envision the host lifting the degeneracy in the absence of an additional ligand or two. This model would account for the lack of concentration effects and had been postulated.[4] However, lifting of the metal porphine degeneracy would split each degenerate metal porphine transition into two not four transitions as is observed. To account for the appearance of more than two transitions one must postulate the existence of different host sites in the matrix. This seems unlikely since the observed splittings are quite similar in three very different matrices. Also, if guest–host interactions

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(14) J. Webb and E. B. Fleischer, *J. Chem. Phys.*, **43**, 3100 (1965).

(15) E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).

(16) D. E. Williams, *J. Chem. Phys.*, **45**, 3730 (1966).

(17) T. Ooi, R. A. Scott, G. Vanderskooi, and H. Scheraga, *J. Chem. Phys.*, **46**, 4410 (1967).

are responsible for the splittings, one would expect the greatest effect with the NH_3 matrix since it is capable of the strongest interactions, but this was not observed. No vapor phase data on porphines are available, but dimerization of copper and zinc phthalocyanines in benzene solution has been reported.[18]

Conclusion

Matrix-isolated free base porphine shows a complex visible spectrum and the split Soret predicted by the theory.[12] All of the features present in the visible matrix spectrum are "more or less" present in the room-temperature solution spectrum as peaks, shoulders, or inflections. The ZnP and CuP exhibit quasiline spectra in matrices of Ar, *n*-octane, and SF_6 but not in NH_3. To explain all our observations, we proposed that these quasilines are not vibronic but result from Davydov splitting of molecular states in metal porphine pairs.

Appendix

Splittings are calculated in the dipole approximation as follows. The interaction integral $(\phi/V/\phi)$ may be expanded in a series of interaction terms between point multiples.[19] The first term is the dipole-dipole term and depends on the inverse cube of the intermolecular distance between centers and on the square of the free molecule transition moment. For strong transitions, the first term dominates the other higher multipole terms and the series may be approximated by it. It has the following form[19]

$$\frac{e^2M^2}{r^3}\cos\phi_{1\mathrm{X}}\cos\phi_{2\mathrm{X}} + \cos\phi_{1\mathrm{Y}}\cos\phi_{2\mathrm{Y}} - 2\cos\phi_{1\mathrm{Z}}\cos\phi_{2\mathrm{Z}}$$

where M^2 = the square of transition moment (in square centimeters)e^2, e = the charge of the electron in esu, r = the distance between centers, and ϕ_{iq} = the angle between the transition moment in molecule i and the q axis. M^2 may be calculated from the oscillator strength by the relationship, $f = (1.085 \times 10^{11})M^2$. Oscillator strengths determined by the relationship[20] $f = 4.33 \times 10^{-9} \int\epsilon(\gamma)\mathrm{d}\gamma$ were found to be 0.60 for ZnP Soret and 0.71 for CuP.

The Hamiltonian for the pair, H, is expressed as a sum of the free molecule Hamiltonian, H, and the potential operator V, which is treated as a perturbation. If the ith molecule ground state wave function is written as ${}^i\phi_{\mathrm{g}}$ and the q excited state wave function as ${}^i\phi_{\mathrm{q}}$, then the wave functions for the pair may be written as follows

$$\psi_{\mathrm{g}} = {}^1\phi_{\mathrm{g}}{}^2\phi_{\mathrm{g}}$$

$$\psi_{\mathrm{e}} = c_1({}^1\phi_{\mathrm{g}}{}^2\phi_{\mathrm{X}}) + c_2({}^2\phi_{\mathrm{g}}{}^1\phi_{\mathrm{X}}) + c_3({}^1\phi_{\mathrm{g}}{}^2\phi_{\mathrm{Y}}) + c_4({}^2\phi_{\mathrm{g}}{}^1\phi_{\mathrm{Y}})$$

where ${}^i\phi_{\mathrm{X}}$ and ${}^i\phi_{\mathrm{Y}}$ are wave functions for the X and Y states. The following secular equation is obtained

$$\begin{vmatrix} X_{\mathrm{X}}{}^{11} - E & I_{12}{}^{\mathrm{X}} & 0 & 0 \\ I_{12}{}^{\mathrm{X}} & X_{\mathrm{X}}{}^{22} - E & 0 & 0 \\ 0 & 0 & X_{\mathrm{Y}}{}^{11} - E & I_{12}{}^{\mathrm{Y}} \\ 0 & 0 & I_{12}{}^{\mathrm{Y}} & X_{\mathrm{Y}}{}^{22} - E \end{vmatrix} = 0$$

where $X_{\mathrm{q}}{}^{ii} = w + ({}^s\phi_{\mathrm{g}}{}^i\phi_{\mathrm{q}}/V/{}^s\phi_{\mathrm{g}}{}^i\phi_{\mathrm{q}})$; w = free molecule excited state energy; $s = 1 + \delta_{1i}$; i = 1 or 2; $(\phi/V/\phi) = \iiint V\phi\,\mathrm{d}\tau$; $I_{12}{}^{\mathrm{q}} = {}^1\phi_{\mathrm{g}}{}^2\phi_{\mathrm{q}}/V/{}^2\phi_{\mathrm{g}}{}^1\phi_{\mathrm{q}})$. Pair excited state energies are found to be $X_{\mathrm{X}} \pm I_{12}{}^{\mathrm{X}}$ and and $X_{\mathrm{Y}} \pm I_{12}{}^{\mathrm{Y}}$. The ground state pair energy is given by

$$E_{\mathrm{g}} = w_{\mathrm{g}} + ({}^1\phi_{\mathrm{g}}{}^2\phi_{\mathrm{g}}/V/{}^1\phi_{\mathrm{g}}{}^2\phi_{\mathrm{g}})$$

Transition energies, $E - E_{\mathrm{g}}$, are calculated to be

$$\Delta E = \Delta w + D^{\mathrm{X}} \pm I_{12}{}^{\mathrm{X}}$$

$$\Delta E = \Delta w + D^{\mathrm{Y}} \pm I_{12}{}^{\mathrm{Y}}$$

$$\Delta w = \text{free molecule transition energy}$$

$$D^{\mathrm{q}} = ({}^s\phi_{\mathrm{g}}{}^1\phi_{\mathrm{q}}/V/{}^s\phi_{\mathrm{g}}{}^1\phi_{\mathrm{q}}) - ({}^1\phi_{\mathrm{g}}/V/{}^1\phi_{\mathrm{g}}{}^2\phi_{\mathrm{g}})$$

D may be thought of as the change in van der Waals binding energy associated with excitation of one molecule to the q state. No satisfactory calculation of D has thus far been reported. However, as can be seen, it does not affect the splitting of the free molecule transitions (which depends on $I_{12}{}^{\mathrm{q}}$), but it does affect the shift of the split transitions from the free molecule value. In many ways, the treatment presented here resembles that for molecular crystals.[20] Here, the situation is somewhat more complex since one is dealing with degenerate molecular states.

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