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Porphyrins
XIV. Theory for the Luminescent State in VO, Co, Cu Complexes*

ROBERT L. AKE and MARTIN GOUTERMAN

Department of Chemistry, University of Washington, Seattle, Washington 98105

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The normal triplet state of closed shell metal porphyrins becomes a "tripdoublet" and a quartet in systems with one unpaired d electron. Exchange integrals between metal d and porphyrin π-electrons give intensity to the tripdoublet and set the tripdoublet-quartet energy gap. These integrals are evaluated theoretically giving tripdoublet radiative lifetimes between 26 and 1450 µsec and tripdoublet-quartet energy gaps in the range 156 to 639 cm^{-1} for the metals and porphyrin skeletons considered. Spin-orbit coupling similarly gives intensity to the quartet and causes a zero field splitting dependent on a parameter Z which has value 0.7, 3.5, 20.4, 21.6 cm^{-1} for Zn (triplet), Cu, Co and VO complexes. Theory predicts that the intensity ratio of 0–1 to 0–0 bands will be very low for the tripdoublet but stronger for the quartet. Existing experimental evidence shows that luminescence comes from both the tripdoublet and the quartet states, their relative importance varying with metal, porphyrin skeleton, and temperature.

Der normale Triplett-Zustand eines metallischen Porphyrins mit abgeschlossener Elektronenschale spaltet in Systemen mit einem ungepaarten d-Elektron in ein „Triplett-Dublett" und ein Quartett auf. Das Auftreten von Austauschintegralen zwischen Metall-d-Elektronen und den π-Elektronen des Porphyrins ist verantwortlich für die Energielücke zwischen dem „Triplett-Dublett"- und dem Quartett-Zustand. Die theoretische Berechnung dieser Integrale liefert für den „Triplett-Dublett"-Zustand Zerfallszeiten zwischen 26 und 1450 µsec und „Triplett-Dublett"-Quartett-Energieabstände in dem Bereich zwischen 156 und 639 cm^{-1} für die betrachteten Metall- und Porphyringerüste. Die Spin-Bahn-Kopplung verursacht eine Nullfeld-Aufspaltung, die von einem Parameter Z abhängt, der für Zn-(Triplett), Cu-, Co- bzw. VO-Komplexe die Werte 0,7; 3,5; 20,4 bzw. 21,6 cm^{-1} annimmt. Die Theorie sagt vorher, daß das Intensitätsverhältnis der 0–1-Bande zur 0–0-Bande sehr klein sein wird für das „Triplett-Dublett", etwas größer dagegen für das Quartett. Das Experiment zeigt, daß Lumineszenz von beiden Zuständen möglich ist, ihre relative Stärke jedoch mit dem Metall, dem Porphyringerüst und der Temperatur variiert.

L'état triplet normal d'une porphyrine métallique à couches complètes devient un «tripdoublet» et un quartet dans les systèmes avec un électron d non apparié. Les intégrales d'échange entre les électrons d du métal et π de la porphyrine donnent l'intensité du tripdoublet et assurent la différence énergétique entre le tripdoublet et le quartet. Ces intégrales sont calculées théoriquement et l'on obtient un temps de vie radiative du tripdoublet entre 26 et 1450 µsec et une séparation tripdoublet-quartet dans la zone de 156 à 639 cm^{-1} pour les composés considérés. Le couplage spin-orbite donne de la même manière son intensité au quartet et provoque une séparation à champ nul dépendant d'un paramètre Z dont les valeurs sont 0.7; 3.5; 20.4; 21.6 cm^{-1} pour les complexes avec Zn (triplet), Cu, Co et VO. La théorie prédit que le rapport des intensités des bandes 0–1 et 0–0 saer très faible pour le tripdoublet et plus fort pour le quartet. Les faits expérimentaux existants montrent que la luminescence provient des deux états, avec une importance variable selon le métal, le squelette porphyrique et la température.

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1. Introduction

Previous papers in this series have concerned themselves with various aspects of the electronic spectra of porphyrins, both theoretical and experimental. In particular Paper I reviewed experimental features, Paper III calculated the π-electron energy levels from Pariser-Parr-Pople theory. Papers IV, V, VI, VIII, X used extended Hückel (EH) theory to describe the effect of metals on the electronic structure [1]. This paper consider in detail the influence of a single unpaired d electron on the luminescence properties of VO, Co, Cu complexes.

As will be seen, the problem of this paper involves detailed consideration of the coulombic interaction of porphin π- and metal d-electrons, which will be taken up in Section 2, where the electronic states and their couplings are considered. However, an understanding of the experimental findings requires, in addition, consideration of vibronic and spin interactions, which are taken up in Sections 3 and 4. Finally in Section 5 we compare the theory to existing experimental data. The two Appendices consider the sensitivity of our results to parameter variation and the effect of pyridine complex formation.

We might point out that the general problem is strongly reminiscent of the problem of oxygen effects on triplet benzene luminescence, which has been considered theoretically by Murrell [2] and Hoijtinck [3]. The porphyrin calculation is more easily handled because the complex geometry has high symmetry and is known from X-ray studies.

2. Electronic States and Coulomb Coupling

A. Basic Theory

Let us begin by consideration of a two electron molecule with non-degenerate orbitals labeled a^0, b^0, complexed with a one electron perturber with a single orbital labeled m^0. In the complex there will be a certain amount of mixing, but we shall suppose the orbitals can be associated to those in the uncomplexed case so that the names a, b, m, can still be used. In the uncomplexed case the ground state will be

$$ {}^1\psi_0 = |a^0\bar{a}^0| \,, \tag{1} $$

while the excited configuration a^0b^0 gives rise to four states

$$ \begin{aligned} {}^1\psi_1 &= \{|a^0\bar{b}^0| - |\bar{a}^0 b^0|\}/\sqrt{2}\,, \\ {}^3\psi_1 &= \begin{cases} |a^0 b^0| \\ \{|a^0\bar{b}^0| + |\bar{a}^0 b^0|\}/\sqrt{2} \\ |\bar{a}^0\bar{b}^0|\,. \end{cases} \end{aligned} \tag{2} $$

In this a^0, $\bar{a}^0$ refer to spin orbitals with opposite spin and $|a^0\bar{a}^0|$, etc. refer to Slater determinants. In the complex the ground state will be

$$ {}^2\psi_0 = \begin{cases} |a\bar{a}m| \\ |a\bar{a}\bar{m}|\,, \end{cases} \tag{3} $$

while the excited configuration *abm* gives rise to eight states, which in zeroth order are conveniently represented by

$$
\begin{aligned}
{}^2\psi_1 &= \begin{cases} \{|a\bar{b}m| - |\bar{a}bm|\}/\sqrt{2} \\ \{|a\bar{b}\bar{m}| - |\bar{a}b\bar{m}|\}/\sqrt{2}, \end{cases} \\
{}^2\psi_2 &= \begin{cases} \{2|ab\bar{m}| - |a\bar{b}m| - |\bar{a}bm|\}/\sqrt{6} \\ \{|a\bar{b}\bar{m}| + |\bar{a}b\bar{m}| - 2|\bar{a}\bar{b}m|\}/\sqrt{6}, \end{cases} \\
{}^4\psi_1 &= \begin{cases} |abm| \\ \{|ab\bar{m}| + |a\bar{b}m| + |\bar{a}bm|\}/\sqrt{3} \\ \{|a\bar{b}\bar{m}| + |\bar{a}b\bar{m}| + |\bar{a}\bar{b}m|\}/\sqrt{3} \\ |\bar{a}\bar{b}\bar{m}|. \end{cases}
\end{aligned}
\tag{4}
$$

We shall call ${}^2\psi_1$ the *singdoublet* and ${}^2\psi_2$ the *tripdoublet*.

The energies of these states above that of the ground state are given below

$$
\begin{aligned}
E({}^2\psi_1) - E({}^2\psi_0) &= \varepsilon_b - \varepsilon_a - J_{ab} + 2K_{ab} \\
&= ES1, \\
E({}^2\psi_2) - E({}^2\psi_0) &= \varepsilon_b - \varepsilon_a - J_{ab} + K_{am} + K_{bm} \\
&= ET1 + K_{am} + K_{bm} = ED1, \\
E({}^4\psi_1) - E({}^2\psi_0) &= \varepsilon_b - \varepsilon_a - J_{ab} - \frac{1}{2}(K_{am} + K_{bm}) \\
&= ET1 - \frac{1}{2}(K_{am} + K_{bm}) = EQ1,
\end{aligned}
\tag{5}
$$

where the ε_i refer orbital energies which can be expressed in terms of one and two electron integrals, and the J_{ij} and K_{ij} are Coulomb and exchange integrals defined as follows

$$
\begin{aligned}
J_{ij} &\equiv J(ij) \equiv (ij \mid ij) = \int i^*(1) j^*(2) (e^2/r_{12}) i(1) j(2) \, d\tau_{12}, \\
K_{ij} &\equiv K(ij) \equiv (ij \mid ji) = \int i^*(1) j^*(2) (e^2/r_{12}) j(1) i(2) \, d\tau_{12}.
\end{aligned}
\tag{6}
$$

It is seen that the singdoublet ${}^2\psi_1$ has approximately the energy of a normal closed shell singlet, while ${}^2\psi_2$ and ${}^4\psi_1$ have an average energy of the normal excited triplet but are split by energies dependent on the exchange integrals between orbitals on the substrate and perturber.

Radiative transitions ${}^2\psi_0 \to {}^2\psi_1$ and ${}^2\psi_0 \to {}^2\psi_2$ are both spin allowed, but it is easy enough to show that the transition dipole to the singdoublet, which we call $\boldsymbol{q}_{ab}$, is essentially that of the uncomplexed ${}^1\psi_0 \to {}^1\psi_1$, while ${}^2\psi_0 \to {}^2\psi_2$ is forbidden. However, because of electronic interaction, there is a coupling term

$$
({}^2\psi_1 \mid e^2/r_{12} \mid {}^2\psi_2) = (3/4)^{1/2} (K_{bm} - K_{am}). \tag{7}
$$

If $\boldsymbol{q}_{ab} \neq 0$ the tripdoublet will gain some intensity through the interaction with the singdoublet. If the energy separation between the two doublets is large compared to the interaction energy, perturbation theory gives the new wave functions

$$
{}^2\psi_2' = {}^2\psi_2 + \frac{\sqrt{3}}{2} \, \frac{(K_{bm} - K_{am})}{\Delta E_{12}} \, {}^2\psi_1, \tag{8}
$$

where $\Delta E_{12} = E(^2\psi_1) - E(^2\psi_2)$. The transition dipole is now

$$(^2\psi_0 \,|\, \boldsymbol{er} \,|\, ^2\psi_2') = \frac{\sqrt{3}}{2} \, \frac{(K_{bm} - K_{am})}{\Delta E_{12}} \, \boldsymbol{q}_{ab} \,. \tag{9}$$

The intensity of the absorption, which is proportional to the square of the transition dipole, is

$$\begin{aligned} I_{02} &\sim \frac{3}{4} \left| \frac{K_{bm} - K_{am}}{\Delta E_{12}} \right|^2 \boldsymbol{q}_{ab}^2 \\ &= \frac{3}{4} \left| \frac{K_{bm} - K_{am}}{\Delta E_{12}} \right|^2 (E_2/E_1)\, I_{01} \,, \end{aligned} \tag{10}$$

where I_{01} is the intensity of the singdoublet measured by the oscillator strength. Unless the two exchange integrals are equal, I_{02} should be non-vanishing. Thus the effect of complex formation is to create a state having approximately the energy of the triplet state but which is no longer spin forbidden.

This basic theory, previously applied to oxygen-benzene complexes [2, 3] can be applied to porphyrins. However, as we shall now see, because of configuration interaction and degeneracy in the uncomplexed porphin, four times as many states must be considered and the problem is rather more complicated.

B. Theory Applied to Porphyrins

Previous papers in this series [1] have shown that the principal absorption bands of metalloporphyrins for $\lambda \gtrsim 3600$ Å arise from transitions between top filled orbitals a_{2u}, a_{1u} and lowest empty orbitals e_{gx}, e_{gy}. The former two are approximately degenerate, while the latter two are rigorously so. The closed shell metals will therefore have four times as many low lying excited states as indicated in Eq. (2), but these occur in degenerate pairs. We can denote the excited states associated with the transition $a_{1u} \rightarrow e_g$ as $^1\psi_1$ and $^3\psi_1$ and those associated with $a_{2u} \rightarrow e_g$ as $^1\psi_2$ and $^3\psi_2$. These states will have forms analagous to Eq. (2) and have been written out else where [7]. Their energies will be denoted $ES1$, $ET1$, $ES2$, $ET2$ in analogy to Eq. (5). The transition dipoles $(^1\psi_0 \,|\, \boldsymbol{er} \,|\, ^1\psi_1) \approx (^1\psi_0 \,|\, \boldsymbol{er} \,|\, ^1\psi_2)$, and we shall in this study assume they are exactly equal to $\boldsymbol{R}_q$. The two singlets mix heavily under CI since they are nearly degenerate. The new states thus formed are the highly allowed ^1B and the relatively weaker ^1Q, their energy difference being 6000–7000 cm^{-1}. The triplets do not mix for group theoretical reasons and remain pure configurations. It will be found later to be computationally convenient to construct the Hamiltonian in terms of the pure configuration functions for both the singlets and triplets.

We shall be concerned with the metal complexes VO, Co, Cu. Previous theoretical and experimental work [4, 5, 6] has established that the unpaired electron in these systems occupies an orbital $b_{2g}(d_{xy})$, $a_{1g}(d_{z^2})$, $b_{1g}(d_{x^2-y^2})$ respectively[1]. For each of these, ground states analogous to Eq. (3) can be written and excited states analogous to Eq. (4). The doublets and quartets arising from the transition

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[1] We shall use the group theoretical labels of D_{4h} to designate orbitals in such systems as the VO complex, which has lower symmetry, whenever the orbital can be correlated with one in a system with the higher symmetry.

$a_{1u} \rightarrow e_g$ we shall call ${}^2\psi_1$, ${}^2\psi_3$, ${}^4\psi_1$, and those arising from $a_{2u} \rightarrow e_g$ we shall call ${}^2\psi_2$, ${}^2\psi_4$, ${}^4\psi_2$. In this the allowed "singdoublets" are ${}^2\psi_1$ and ${}^2\psi_2$ with energies $ES1$ and $ES2$; the nearly forbidden "tripdoublets" are ${}^2\psi_3$ and ${}^2\psi_4$ with energies $ED1$ and $ED2$; the quartets are ${}^4\psi_1$ and ${}^4\psi_2$ with energies $EQ1$ and $EQ2$. These energies can be expressed analogously to Eqs. (4) and (5) and are written out elsewhere [7]. The transition dipoles for the doublet-doublet transitions are

$$\begin{aligned} ({}^2\psi_0 \,|\, er \,|\, {}^2\psi_1) &= ({}^2\psi_0 \,|\, er \,|\, {}^2\psi_2) = \boldsymbol{R}_q\,, \\ ({}^2\psi_0 \,|\, er \,|\, {}^2\psi_3) &= ({}^2\psi_0 \,|\, er \,|\, {}^2\psi_4) = 0\,. \end{aligned} \tag{11}$$

The tripdoublets have no intensity while the singdoublets, which give rise to the B and Q bands, have the same intensity as they had in the absence of the odd electron.

Although perturbation theory was used in the previous section to find the new wavefunction, it is more convenient in the case of porphyrins to diagonalize the Hamiltonian matrix on a basis set of the doublet wave functions just defined. All the interactions are either through exchange terms or are zero. The situation is therefore one of conducting a limited inter- and intraconfiguration CI treatment. The exchange interactions take the form shown in Eq. (7). The matrix factors into identical x and y polarized submatrices, the first of which is

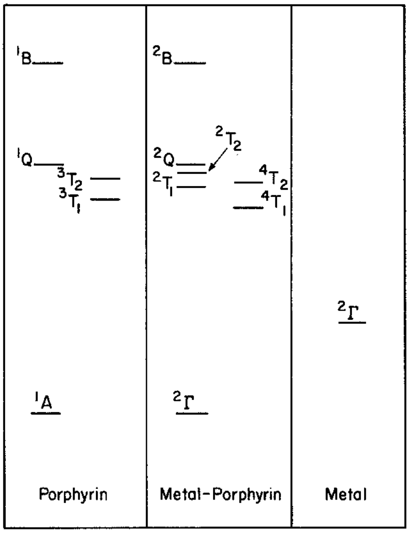

Fig. 1. Energy level diagram showing the effect on a closed shell porphyrin of an odd electron in an orbital of symmetry Γ

$$\begin{array}{c|cccc} & {}^2\psi_1 & {}^2\psi_2 & {}^2\psi_3 & {}^2\psi_4 \\ \hline {}^2\psi_1 & ES1-\lambda\beta_{1g} & \mathrm{CI} & K'(\sigma,\pi) & 0 \\ {}^2\psi_2 & \mathrm{CI} & ES2+\lambda\beta_{1g} & 0 & K''(\sigma,\pi) \\ {}^2\psi_3 & K'(\sigma,\pi) & 0 & ED1-\lambda\beta_{1g} & 0 \\ {}^2\psi_4 & 0 & K''(\sigma,\pi) & 0 & ED2+\lambda\beta_{1g} \end{array} \tag{12}$$

where

$$\mathrm{CI} = 2 \int e_{gy}^{*}(1)\, a_{2u}^{*}(2)\, (e^2/r_{12})\, a_{1u}(1)\, e_{gx}(2)\, \mathrm{d}\tau_{12}\,,$$

$$K'(\sigma, \pi) = (3/4)^{1/2}\,[K(e_g, b_{1g}) - K(a_{1u}, b_{1g})]\,,$$

$$K''(\sigma, \pi) = (3/4)^{1/2}\,[K(e_g, b_{1g}) - K(a_{2u}, b_{1g})]\,.$$

(The significance of $\lambda\beta_{1g}$ will be explained in Section 3 and can be ignored in this section.)

The Matrix (12) shows zero elements that are rigorous. Our problem then is to evaluate the non-zero elements. Methods of evaluation will be taken up in the next section. The higher energy tripdoublet will have the wave function

$$^2\psi_3' = C_{31}\,{}^2\psi_1 + C_{32}\,{}^2\psi_2 + C_{33}\,{}^2\psi_3 + C_{34}\,{}^2\psi_4 \tag{13}$$

with transition dipoles

$$(^2\psi_0 \mid e\boldsymbol{r} \mid {}^2\psi_3') = (C_{31} + C_{32})\, \boldsymbol{R}_q\,. \tag{14}$$

The contribution from $^2\psi_1$ and $^2\psi_2$ can interfere constructively or destructively depending on the relative signs of C_{31} and C_{32}. The intensity of the lower energy tripdoublet depends analogously on C_{41} and C_{42}. A schematic energy level diagram is given in Fig. 1.

C. Matrix Element Evaluation

(i) *σ-π-Exchange Integrals*

There are three principal types of contribution to the $K(\sigma, \pi)$ integrals: (1) one-center terms that arise from d orbital delocalization into the ring and π-delocalization onto the metal; (2) two-center d-π-terms; (3) in Cu, two center N(2s, 2$p\sigma$) − C(2$p\pi$) terms, which are sizeable because of the extensive $d_{x^2-y^2}$ delocalization. A more detailed discussion of these terms is given elsewhere [7].

The two center d-π-exchange integral was calculated from a program written by R. M. Stevens and R. K. Nesbet [8] using the exponents determined by Zerner [1c] for the extended Hückel model and the geometry of nickel etioporphyrin [9]. The Zerner exponents seemed most appropriate as they were those single exponents that best reproduced nitrogen-metal overlap integrals when these are calculated from accurate many term wave functions.

The one center integrals can be expressed in terms of Slater-Condon integrals commonly denoted F^k and G^k, which arise when r_{12}^{-1} is expanded in Legendre polynomials [10]. Some of these integrals can be obtained from the energy differences of certain atomic or ionic spectral lines, but the great majority are not well known. We used the experimental values for the best known radial integrals to determine an exponential constant, ζ_{eff}, which could then be used to calculate the remaining Slater-Condon integrals. The resulting ζ_{eff} are given elsewhere [7].

Thus the necessary $K(\sigma, \pi)$ integrals are obtained using EH orbital coefficients to expand molecular orbitals in terms of atomic orbitals. One center atomic orbital integrals are obtained using reduced exponents such as fit atomic states, and certain larger two center integrals are included and evaluated from programs using EH orbital exponents. The results in Tables 1 and 2 show that the one center contributions dominate.

Table 1. *One center contributions to σ-π-exchange integral in cm^{-1}*

Integral	Metal	Porphyrin	Total
$K_0(b_{1g}, e_g)$Cu	11.0	339.8	350.8
$K_0(b_{1g}, a_{2u})$Cu	3.6	565.1	568.7
$K_0(b_{1g}, a_{1u})$Cu	0.0	36.6	36.6
$K_0(a_{1g}, e_g)$Co	225.3	7.2	232.5
$K_0(a_{1g}, a_{2u})$Co	131.1	7.6	138.7
$K_0(a_{1g}, a_{1u})$Co	0.0	3.5	3.5
$K_0(b_{2g}, e_g)$VO	386.2	7.6	393.8
$K_0(b_{2g}, a_{2u})$VO	110.4	6.0	116.4
$K_0(b_{2g}, a_{1u})$VO	0.0	11.9	11.9

(ii) *Diagonal Energies and* CI *Matrix Elements*

The energies $ES1$, $ES2$, and CI of Matrix (12) will be obtained from previous analysis of porphyrin spectra [12]. We define an allowed and forbidden state

$$\begin{aligned} B_x^0 &= (\psi_{1x} + \psi_{2x})/\sqrt{2}\,, \\ Q_x^0 &= (\psi_{2x} - \psi_{1x})/\sqrt{2}\,. \end{aligned} \tag{15}$$

In any particular case, the excited states can be expressed

$$\begin{aligned} B_x &= \cos\theta B_x^0 + \sin\theta Q_x^0\,, \\ Q_x &= -\sin\theta B_x^0 + \cos\theta Q_x^0\,. \end{aligned} \tag{16}$$

The absolute value of θ can be obtained from

$$I(Q_x)/I(B_x) = (\nu_Q/\nu_B)\tan^2\theta\,. \tag{17}$$

The values of $ES1$, $ES2$, CI can be obtained from

$$\begin{aligned} ES1 + ES2 &= E(B) + E(Q) \\ ES1 - ES2 &= \sin 2\theta[E(B) - E(Q)] \\ \mathrm{CI} &= \cos 2\theta[E(B) - E(Q)]\,. \end{aligned} \tag{18}$$

The ambiguity of sign for θ was resolved earlier [1a, 12]. In Ni and Co tetraphenylporphin (TPP) the ratio of Eq. (17) is nearly zero while in Ni and Co octalkylporphin (OAP) the ratio is finite. However, since the alkyl groups should lower the energy of $a_{1u} \rightarrow e_g(ES1)$ relative to $a_{2u} \rightarrow e_g(ES2)$, the sign of θ is thereby

Table 2. *The total σ-π exchange integral in cm^{-1}*

Integral	Copper	Cobalt	Vanadyl
$K(d^*, e_g)$	396.0	238.3	460.1
$K(d^*, a_{1u})$	95.5	3.5	11.9
$K(d^*, a_{2u})$	587.3	147.7	271.6

d^* is the molecular orbital of the unpaired electron.

Table 3. *Experimental energy and intensity parameters and calculated ES 1 and ES 2 values*[a]

Compound	Experimental				Calculated		
	f_B	f_Q	$\tilde{\nu}_B$	$\tilde{\nu}_Q$	$ES2(a_{2u}e_g)$	$ES1(a_{1u}e_g)$	CI
Vanadyl Deutero	1.015	0.050	24540	17530	22757	19313	3053
Vanadyl TPP	1.09	0.0143	23310	16950	19291	20969	3067
Cobalt Deutero	1.10	0.077	25510	18210	23942	19778	2998
Cobalt TPP	1.22	0.000	24131	17704	20918	20918	3213
Copper Deutero	1.093	0.058	25160	17870	23369	19661	3138
Copper TPP	1.370	0.006	24000	17300	20131	21169	3310

[a] Entries in the first four columns were taken from Ref. [13]. Deuteroporphyrin (Ref. [13a]) with six alkyls has been used as its spectra were consistently tabulated and differ very little from octalkylporphin (OAP).

determined. The necessary spectral values and the resulting calculated values are given in Table 3. In these metal complexes the excited states calculated are, of course, singdoublets not singlets.

Finally $ED1$ and $ED2$ are needed to complete Matrix (12). Eq. (5) shows that these can, for Cu, be written

$$\begin{aligned} ED1 &= ES1 - 2K(a_{1u}, e_g) + K(a_{1u}, b_{1g}) + K(e_g, b_{1g}), \\ ED2 &= ES2 - 2K(a_{2u}, e_g) + K(a_{2u}, b_{1g}) + K(e_g, b_{1g}) \end{aligned} \tag{19}$$

and similarly for Co and VO. The last two integrals of Eqs. (19) are of type $K(\sigma, \pi)$ whose evaluation was discussed above. The other exchange integral is a π-π type and was evaluated from the MO's obtained from the EH programs. The $K(\pi, \pi)$ were evaluated like the $K(\sigma, \pi)$ keeping all one and two-center integrals and using reduced exponential constants. This method has been suggested by Lykos [14].

The resulting energies obtained for the tripdoublet states are given in the top part of Table 4. The energies are far lower than observed luminescences suggesting

Table 4. *Calculated energies of tripdouplets and quartets*

		VO Deutero[c]	VO TPP	Co Deutero	Co TPP	Cu Deutero	Cu TPP	Cu[a] P	Cu[b] P
	$K(a_{2u}, e_g)$	6047	6047	7407	7407	7660	7660	7660	7660
	$K(a_{1u}, e_g)$	5397	5397	5765	5765	6016	6016	6016	6016
I	${}^2E_u(a_{2u}e_g)$	11395	7929	9514	6490	9032	5794	8608	6199
	${}^2E_u(a_{1u}e_g)$	8991	10647	8490	9630	8121	9629	8996	11405
	$K(a_{2u}, e_g)$	3060	3060	3192	3192	3317	3317	3317	3317
	$K(a_{1u}, e_g)$	2731	2731	2485	2485	2605	2605	2605	2605
	${}^2E_u(a_{2u}e_g)$	17013	13540	17716	14693	17159	13923	16738	14328
II	${}^4E_u(a_{2u}e_g)$	16458	12985	17467	14443	16523	13284	16099	13689
	ΔE_{DQ}	555	555	250	250	639	639	639	639
	${}^2E_u(a_{1u}e_g)$	(14095)	15745	(14908)	16048	(14665)	16173	15537	17949
	${}^4E_u(a_{1u}e_g)$	13737	15387	14752	15892	14346	15854	15218	17630
	ΔE_{DQ}	358	358	156	156	319	319	319	319

I. Based on $K(\sigma, \pi)$ and $K(\pi, \pi)$ calculated with reduced exponentials.

II. Based on integrals further scaled to match the emission energies given in parentheses, see text.

[a] Assumes $(a_{1u}e_g)$ lower. — [b] Assumed $(a_{2u}e_g)$ lower. — [c] See footnote to Table 3.

that in spite of the reduction of exponents the exchange integrals in Eq. (19) are overestimated. If the sum of exchange integrals in Eq. (19) is reduced by a factor 0.506, 0.431, 0.433 for VO, Co, Cu then the reported luminescences in mesoporphyrin, a porphyrin with an octalkylporphin type spectrum, can be fit [15]. The resultant energies are given in the second part of Table 4.

Since the same $K(\sigma, \pi)$ integrals that enter into $ED1$ and $ED2$ also determine $EQ1$ and $EQ2$, these latter can also be calculated. Using the same scaling factors, we have used these integrals to estimate the quartet energies, which are also given in Table 4.

An intersting point now occurs. We notice that in the TPP complexes the tripdoublet $^2T(a_{2u}e_g)$ is lower and has a large doublet-quartet energy gap, while in the octalkyl series the tripdoublet $^2T(a_{1u}e_g)$ is lower with a far smaller doublet-quartet gap. This difference relates to the character of a_{2u} and a_{1u}. The a_{2u} orbital has density on the N atoms and so has a large $K(\sigma, \pi)$ integral while the a_{1u} orbital has density on the exopyrrole positions and is raised in energy by the alkyl groups. The experimental energy of the CuTPP luminescence is 13,300 cm^{-1} and we tentatively ascribe it to the quartet state in agreement with the prediction in Table 4. An indirect corroboration of this assignment is that the method predicted a triplet energy for ZnTPP of 12,795 cm^{-1}. A Russian emission spectrum [16] shows phosphorescence to be at 12,820 cm^{-1}.

D. Radiative Tripdoublet Results

Table 5 gives the final expected intensities and radiative lifetimes calculated by the method presented above: (i) Experimental absorption values determine $ES1$, $ES2$, and CI in Matrix (12); (ii) the $K(\sigma, \pi)$ integrals are calculated, but are scaled along with $K(\pi, \pi)$ so that $ED1$ and $ED2$ fit the experimental luminescence energy; (iii) experimental values are used for the allowed oscillator strengths. The f values were converted to rough extinction coefficients by assuming the band widths of the Q_{0-0} and the tripdoublet are the same and using the expression

$$f = 4.33 \times 10^{-9} \varepsilon \Delta \tilde{\nu}\,, \tag{20}$$

Table 5. *Oscillator strengths, absorption coefficients, and radiative lifetimes for the tripdoublets*

Compound	Higher tripdoublet			Lower tripdoublet		
	f	$\varepsilon_{\max}$[a] (*l*/mole cm)	τ_1[b] (μsec)	f	$\varepsilon_{\max}$[a] (*l*/mole cm)	τ_1[b] (μsec)
VO Deutero[c]	8.71×10^{-5}	40	60	2.91×10^{-4}	134	26
VO TPP	4.13×10^{-5}	19	147	3.76×10^{-5}	16	217
Co Deutero	2.81×10^{-5}	13	170	8.04×10^{-5}	37	84
Co TPP	4.77×10^{-5}	22	122	4.78×10^{-6}	2	1450
Cu Deutero	2.52×10^{-5}	12	202	1.19×10^{-4}	55	59
Cu TPP	3.21×10^{-5}	15	179	2.75×10^{-5}	13	281

[a] $\varepsilon_{\max}$ calculated from f assuming $\Delta\tilde{\nu}_{1/2} = 500$ cm^{-1} in Eq. (26).

[b] τ_1 calculated from f using Eqs. (26) and (27) and $\tilde{\nu}$ values from Table 6. We take $n^2(g_l/g_u) = 1$ in Eq. (27).

[c] See footnote to Table 3.

where ε is the maximum molar extinction coefficient in (moles cm/liter)$^{-1}$ and $\Delta\tilde{\nu}$ is the band width at half maximum in cm^{-1}. The lifetimes for the individual tripdoublet states were obtained through use of the expression [17]

$$\tau_1^{-1} = 2.880 \times 10^{-9} n^2 (g_l/g_u)\, \tilde{\nu}^2 \varepsilon \Delta \tilde{\nu}\,, \tag{21}$$

where n is the index of refraction and g_l/g_u is the ratio of lower state to upper state degeneracy. In the actual molecule these electronic radiative lifetimes might conceivably differ from the natural radiative lifetime because of vibronic coupling. This effect will be shown in Section 3 to be small.

We made use of this very empirical approach because we wanted values that would be useful for comparison with experiment. However in addition, we did calculations that obtained the π-electron energies in Matrix (12) from an SCMO-PPP [1b] calculation. Together with the σ-π-exchange integrals of Table 2, they provide a "pure" theoretical alternative to the empirical Hamiltonian just described. These results are tabulated elsewhere [7]. The lower tripdoublets for VO, Co, Cu are predicted to appear respectively at 763, 783, 748 mμ and the tripdoublet-quartet energy gaps are 1100, 580, 1475 cm^{-1}. Oscillator strengths (based on empirical absorption intensities) are respectively 9×10^{-5}, 2×10^{-5}, 10^{-4}. Although these values are quite reasonable, the more empirically determined values of Table 5 would seem to be more useful as a guide to experiment.

The combined strength of the two tripdoublests will depend on the ratio of the σ-π-exchange integral to the π-π-exchange integrals as expressed in Eq. (10). There will also be a strong difference in intensity between the two tripdoublets that depends on the diagonal energies in the Matrix (12). Perturbation theory for f_2 gives

$$f_2 \sim \left| \frac{K}{(ES1-ED2)} - \frac{K \cdot \mathrm{CI}}{(ES1-ED2)(ES2-ED2)} \right|^2 . \tag{22}$$

It follows from Eq. (22) that f_2 is sensitive to parameter choice. Fortunately f_1, the lower energy tripdoublet oscillator strength, is not very sensitive to small variations in the energy parameters $ES1, ES2$, etc., and it is the lower energy state that is observed experimentally.

3. Vibronic Coupling

As discussed earlier, the visible metal porphyrin absorption consists of two principal bands, Q_{0-0} and Q_{0-1}. The latter band arises from vibronic borrowing to which several modes contribute [18]. The oscillator strength of Q_{0-1} is generally comparable to and sometimes greater than that of Q_{0-0}. In calculating the natural radiative lifetime of the tripdoublet it is therefore necessary to find out if vibronic coupling is expected to be of importance.

We shall discuss vibronic coupling in a rather limited context. The Hamiltonian can be expanded in a Taylor series in the normal coordinates Q_i:

$$H = H_0 + \sum_i Q_i (\partial H / \partial Q_i)\,. \tag{23}$$

The coupling terms $\partial H/\partial Q_i$ are one electron and have the symmetry of the mode Q_i. We confine attention to the doublet states arising from the transitions

a_{1u}, $a_{2u} \to e_g$, and we can add to Matrix (12) elements that arise due to the second term of Eq. (23). In addition there will be vibronic terms coupling the four x polarized states of Matrix (12) and the four corresponding y polarized states.

Because of the form of the excited states, the vibronic coupling will arise from the following one electron terms:

$$\begin{aligned}
(a_{2u} \mid V(Q) \mid a_{2u}) &= \lambda_{a2}\alpha_{1g}\,,\\
(a_{1u} \mid V(Q) \mid a_{1u}) &= \lambda_{a1}\alpha_{1g}\,,\\
(a_{2u} \mid V(Q) \mid a_{1u}) &= \lambda_{12}\alpha_{2g}\,,\\
(e_{gx} \mid V(Q) \mid e_{gx}) &= \lambda_e\alpha_{1g} + \lambda_x\beta_{1g}\,,\\
(e_{gy} \mid V(Q) \mid e_{gy}) &= \lambda_e\alpha_{1g} - \lambda_x\beta_{1g}\,,\\
(e_{gx} \mid V(Q) \mid e_{gy}) &= \lambda_{xy}\beta_{2g}\,.
\end{aligned} \tag{24}$$

(Of course these should be a summed over the modes of appropriate symmetry.) The linear terms in the totally symmetric coordinates α_{1g} have the effect of shifting the equilibrium position of the totally symmetric coordinates giving rise to a Franck-Condon progression. However from the vibronic envelope of the strongly allowed B band it is clear that shift is relatively small and the main intensity of Q_{0-1} must have another origin. It originates from the Q and B electronic states mixing under the non-totally symmetric vibrations. These $\lambda\beta_{1g}$ terms appear in Matrix (12).

Since our present purpose is to compare the order of magnitude of vibronic effects in the singdoublets and tripdoublets we shall simplify Matrix (12) by assuming $ES1 = ES2 \equiv ES$ and $K'(\sigma,\pi) = K''(\sigma,\pi) \equiv K$. We then rotate ${}^2\psi_1$ and ${}^2\psi_2$ to remove the large off-diagonal CI integral and obtain

$$\begin{array}{cccc}
{}^2B^0 & {}^2Q^0 & {}^2T_2 \equiv {}^2\psi_3 & {}^2T_1 \equiv {}^2\psi_4 \\
\hline
ES + \mathrm{CI} & \lambda\beta_{1g} & K/\sqrt{2} & -K/\sqrt{2} \\
\lambda\beta_{1g} & ES - \mathrm{CI} & K/\sqrt{2} & K/\sqrt{2} \\
K/\sqrt{2} & K/\sqrt{2} & ED2 + \lambda\beta_{1g} & 0 \\
-K/\sqrt{2} & K/\sqrt{2} & 0 & ED1 - \lambda\beta_{1g}\,.
\end{array} \tag{25}$$

Using perturbation theory we shall see that the vibronic contribution to ${}^2Q^0$ and the ${}^2T$ states will be of a different order of magnitude. If we assume that only the transition $\boldsymbol{\mu}({}^2B^0)$ is non-zero, we have

$$\boldsymbol{\mu}({}^2Q^0) = [\lambda\beta_{1g}/(E_B - E_Q)]\,\boldsymbol{\mu}({}^2B^0)\,, \tag{26}$$

$$\begin{aligned}
\boldsymbol{\mu}({}^2T) &= -[K/\sqrt{2}(E_B - E_D + \lambda\beta_{1g})]\,\boldsymbol{\mu}({}^2B^0)\\
&\approx -[K/\sqrt{2}(E_B - E_D)]\,\boldsymbol{\mu}({}^2B^0)\\
&\quad + [K\lambda\beta_{1g}/\sqrt{2}(E_B - E_D)^2]\,\boldsymbol{\mu}({}^2B^0)\,,
\end{aligned} \tag{27}$$

where $\boldsymbol{\mu}({}^2B^0)$ is the transition dipole for the transition to ${}^2B^0$. From Eq. (26) we see that

$$\frac{I({}^2Q_{0-1})}{I({}^2B_{0-0})} = \frac{\lambda^2\beta_{1g}^2}{(E_B - E_Q)^2}\,\frac{\tilde{\nu}(Q_{0-1})}{\tilde{\nu}(B_{0-0})}\,, \tag{28}$$

while from (27) we see

$$\frac{I(^2T_{0-1})}{I(^2T_{0-0})}=\frac{\lambda^2\beta_{1g}^2}{(E_B-E_D)^2}\,\frac{\tilde{\nu}(T_{0-1})}{\tilde{\nu}(T_{0-0})}\,. \tag{29}$$

The ratios (28) and (29) are of comparable order of magnitude. But since $I(B_{00}) \gg I(T_{00})$ we see that vibronic coupling should be far less important in the tripdoublet.

In point of fact, this is clearly observed experimentally. Luminescence spectra of Cu porphyrins show far smaller ratios of $0-1$ to $0-0$ intensities than do absorption spectra [1 f].

The same order of magnitude effects hold when the situation is considered with more complex couplings introduced by the α_{2g} and β_{2g} modes.

4. Spin Orbit Coupling and Zero-Field Splitting

In our attempt to analyze the luminescence of porphyrins with one odd *d* electron, it becomes of interst to consider the radiative lifetime of the quartet state and its relation to the radiative lifetime of the triplet state in closed shell metals porphyrins such as the zinc complex. The natural radiative lifetime arises from spin-orbit coupling. As we shall see the same type of terms lift the 8 fold degeneracy of ^4E_u, giving rise to a zero-field splitting. (In addition there will be spin-spin contributions to zero field splitting, but these will not be considered here.)

A. Basic Theory

Since vibronic coupling will play a part in this calculation it is necessary to incorporate into the Hamiltonian the dependence of the electronic energy on nuclear displacement [19]. This can be done most conveniently by expanding the Hamiltonian in a Taylor series as a function of the normal coordinates. Thus, to first order in nuclear displacement

$$H=H_0^0+H_{so}^0+\sum_i\{(\partial H/\partial Q_i)_0+(\partial H_{so}/\partial Q_i)_0\}\,Q_i\,. \tag{30}$$

Using the convenient form of perturbation theory and the eigenfunctions of H_0^0 as a basis, we obtain three perturbing terms:

$$\begin{aligned} H(1)&=H_{so}^0\,,\\ H(2)&=\sum_i(\partial H_0/\partial Q_i)_0Q_i\,,\\ H(3)&=\sum_i(\partial H_{so}/\partial Q_i)_0Q_i\,. \end{aligned} \tag{31}$$

These are in order the spin-orbit coupling, vibronic coupling, and spin-vibronic coupling. A new quartet type wave function can be obtained through the couplings provided by these operators. It is written

$$
\begin{aligned}
{}^4\psi_j = {}^4\psi_{j0} + \sum_{k \neq j} (E_{j0} - E_{k0})^{-1} \{ & \langle \psi_{j0} | H(1) | \psi_{k0} \rangle + \langle \psi_{j0} | H(3) | \psi_{k0} \rangle \\
& + \sum_{l \neq j} (E_{j0} - E_{l0})^{-1} (\langle \psi_{j0} | H(1) | \psi_{l0} \rangle \langle \psi_{l0} | H(2) | \psi_{k0} \rangle \\
& + \langle \psi_{j0} | H(2) | \psi_{l0} \rangle \langle \psi_{l0} | H(1) | \psi_{k0} \rangle) \} \, \psi_{k0} \, .
\end{aligned}
\tag{32}
$$

Some terms have been omitted from this expression. $H(2)$ has no spin dependence so there is no first order term from this operator. It is included in second order since the relative sizes are $H(2) \gg H(1) \gg H(3)$.

Of the perturbation terms in Eq. (32), the first introduces intensity into the $0-0$ band while the other two introduce intensity into vibronic bands. Symmetry arguments show that only g (gerade) vibrations will be active in coupling. In general, the metal should make the largest contribution to spin-orbit coupling. However, g vibrations have no amplitude at the center of the ring. For this reason $H(3)$ will be neglected.

Luminescence polarization studies have established in several cases that polarization is in-plane [20]. Since the Q, B states provide a large reservoir for such intensity, mixing with them should be most important. Further, luminescence studies tend to show that the $0-0$ band of the phosphorescence is rather stronger than vibronic bands. For this reason we shall devote Section B to a quantitative discussion of the "inner configuration" mixing introduced by $H(1)$ within the manifold of states $a_{2u}, a_{1u} \rightarrow e_g$. The term $H(1)$ also gives rise to a zero field splitting to be discussed in Section C. Other possible sources of triplet intensity will be discussed in Section D.

B. Inner Configuration Spin-Orbit Coupling

The spin-orbit operator can be written

$$
H_{so} = \sum_i \lambda_i \ell_i \cdot \mathscr{s}_i \, , \tag{33}
$$

where λ_i is a spin independent totally symmetric function of electron i analogous to the atomic $\xi(r)$ of Condon and Shortley [21]. The sum is over all the electrons, and we shall take $\ell \cdot \mathscr{s}$ as dimensionless. The components of the angular momentum operators ℓ transform as rotations. In D_{4h} this is E_g for ℓ_x, ℓ_y and A_{2g} for ℓ_z. However, since the only excited states we are considering are of E_u symmetry, group theoretical arguments show that only matrix elements for ℓ_z will be non-zero. Further consideration of the excited state wave functions shows that these matrix elements will be either $(a_{2u} | \lambda \ell_z | a_{1u})$ or $(e_{gx} | \lambda \ell_z | e_{gy})$. Except for the contribution of certain one-center terms to the second of these, these are matrix elements over π-electron orbitals, for which only small three center terms are non-zero [22]. Since we are interested in the metal enhancement we shall neglect these. As a result $(a_{2u} | \lambda \ell_z | a_{1u}) = 0$ and

$$
iZ \equiv (e_{gx} | \lambda \ell_z | e_{gy}) = \sum_{i,j} \sum_a C_{xi} C_{yj} (\chi_i | \xi_a \ell_{za} | \chi_j) \, . \tag{34}
$$

Table 6. *Spin-orbit coupling integrals* $[Z=\langle e_{gx}|H_{so}|e_{gy}\rangle]$

Compound	Orbital	Coefficient	Spin-orbit constant (cm^{-1})	Z(cm^{-1})
Vanadyl	V $3d_{yz}$	0.3009	142	12.9
	O $2p_y$	0.2448	144	8.6
	V $4p_y$	0.0387	92	0.1
	Total			21.6
Cobalt	Co $3d_{yz}$	0.2066	478	20.4
Copper	Cu $3d_{yz}$	0.0659	800	3.5
Zinc	Zn $3d_{yz}$	0.0242	1100	0.7

In this C_{xi} and C_{yj} are MO coefficients, and the terms $(\chi_i\,|\,\xi_a\ell_{za}\,|\,\chi_j)$ are one center spin-orbit integrals. In Co and Cu only the term $(3d_{xz}\,|\,\xi_a\ell_{za}|3d_{yz})$ contributes to Eq. (34) while for VO there are also contributions from $4p_x$, $4p_y$ on V and $2p_x$, $2p_y$ on O. These integrals were obtained from atomic spectra and reliable calculations [23] as explained elsewhere [7]. Values of Z are given in Table 6.

The Z terms couple the singlets and triplets of closed shell metals as follows:

$$({}^1\psi_{1x}\,|\,H_{so}\,|\,{}^3\psi_{1y})=({}^1\psi_{2y}\,|\,H_{so}\,|\,{}^3\psi_{2x})=iZ/2\,. \tag{35}$$

They couple the doublet and quartet states as

$$\begin{aligned}({}^2\psi_{1x}\,|\,H_{so}\,|\,{}^4\psi_{1y})&=({}^2\psi_{2y}\,|\,H_{so}\,|\,{}^4\psi_{2x})=iZ/\sqrt{6}\,,\\ ({}^2\psi_{3x}\,|\,H_{so}\,|\,{}^4\psi_{1y})&=({}^2\psi_{4y}\,|\,H_{so}\,|\,{}^4\psi_{2x})=-iZ/\sqrt{18}\,.\end{aligned} \tag{36}$$

Other non-zero terms can be obtained from these using the Hermiticity of H_{so}. The resultant $0-0$ oscillator strengths are given in Table 7.

C. Zero-Field Splitting

The non-zero matrix element Z occurring in Eqs. (34–36) also gives rise to zero-field splitting. Examination of the wave functions of a ${}^3E_u$ state shows that an off-diagonal matrix element $iZ/2$ exists between the two $m_s=1$ components and between the two $m_s=-1$ components. This gives rise to a zero field splitting

Table 7. *Results of vibronic-spin-orbit coupling for quartet state intensity*

Compound	Oscillator strength			Radiative lifetimes (sec)
	0–0	0–1	Total	τ_1[a]
VO OAP	2.45×10^{-7}	1.07×10^{-7}	3.52×10^{-7}	0.046
VO TPP	4.10×10^{-7}	1.34×10^{-7}	5.44×10^{-7}	0.032
Co OAP	3.12×10^{-7}	2.66×10^{-7}	5.78×10^{-7}	0.024
Co TPP	2.29×10^{-7}	2.76×10^{-7}	5.05×10^{-7}	0.028
Cu OAP	1.04×10^{-8}	4.13×10^{-9}	1.45×10^{-8}	0.98
Cu TPP	9.88×10^{-9}	4.21×10^{-9}	1.41×10^{-8}	1.20
Zn OAP	3.57×10^{-9}	1.15×10^{-9}	4.72×10^{-9}	3.12
Zn TPP	1.99×10^{-9}	7.51×10^{-10}	2.74×10^{-9}	6.68

[a] τ_1 calculated from f_{tot} using Eqs. (26) and (27) and $\tilde{\nu}$ values from Table 6. We take $n^2(g_l/g_u)=1/2$ in Eq. (27).

with three degenerate pairs of levels located at $Z/2, 0, -Z/2$. Group theoretical arguments show that of these six levels the middle two are x, y polarized, one of the levels at $-Z/2$ is z polarized, and the other three levels are forbidden [7]. The splitting is quite analogous to that in a diatomic $^3\Pi$ level.

The zero-field splitting of the ^2E_u and ^4E_u levels is more complicated. The four singdoublet levels are not split. The four tripdouplet levels are split into two pairs $\pm Z/3$, and both upper and lower pairs are x, y polarized. The eight ^4E_u levels are split into four pairs. The levels with $m_s = \pm 1/2$ are split by energy $\pm Z/6$ while the levels with $m_s = \pm 3/2$ are split by $\pm Z/2$. If the x axis and y axis are not degenerate the splitting is modified as shown in Fig. 2. The levels with $m_s = \pm 1/2$ are x, y polarized. Of the four levels with $m_s = \pm 3/2$, one will be z-polarized and the other three will be forbidden. Group theoretical arguments show that for Cu and VO porphyrin, the allowed level will be part of the higher energy pairs while in Co porphyrin it will be part of the lower energy pairs. The difference depends on the symmetry of the odd d electron [7].

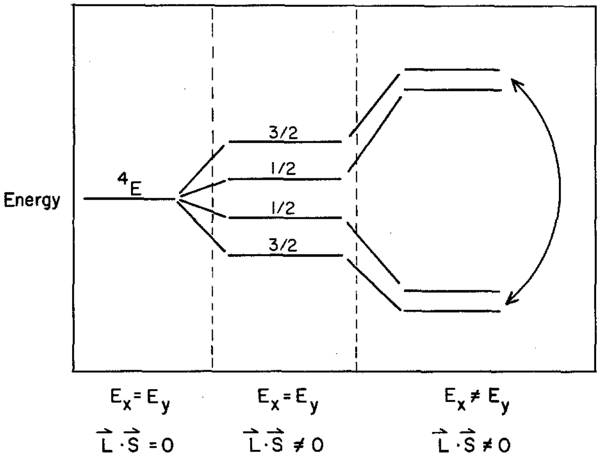

Fig. 2. Zero-field splitting (due to spin-orbit coupling) of a ^4E state for degenerate case ($E_x = E_y$) and for non-degenerate case ($E_x \neq E_y$). Labels are $|m_S|$

D. Other Spin-Orbit Terms and Final Quartet Lifetimes

In addition to the x, y polarized intensity introduced by the methods discussed above, z polarized intensity can be introduced in first order by $H(1)$. We have considered the possible states and conclude that the charge transfer transition $a_{2u} \rightarrow a_{1g}(d_{z^2})$ is the most likely source of z polarized intensity in VO and Co. Although its oscillator strength is small ($\sim 3 \times 10^{-4}$) it has a fairly strong spin-orbit coupling term. It would be more important in Co, where this transition has fairly low energy. It is not present in Cu or Zn where $a_{1g}(d_{z^2})$ is doubly occupied. In Cu some z polarized intensity might be introduced through coupling with the transition $b_{2u}(\sigma) \rightarrow b_{1g}(d_{x^2-y^2})$ which has a transition dipole of 0.1 Å. Quantitative estimates of the size of z polarized intensity is difficult because the EH model does not calculate their intensity properly, and their energies are neither well predicted nor known experimentally.

A detailed account of possible second order routes for vibronic intensity has been given [7]. Referring to Eq. (32), we limit quantitative study to mixing of the quartet state to final states ${}^2\psi_{k0}$ that are either ${}^2Q$ or ${}^2B$. As seen from Eq. (32) there are two vibronic borrowing routes: The intermediate state ψ_{l0} can be either doublet or quartet. Evaluation of the spin orbit integrals of $H(1)$ has been discussed above. The vibronic integrals of $H(2)$ were estimated from the known singlet vibronic coupling. The results are given in Table 7. For VO OAP and CuOAP the borrowing route through the doublet intermediate gave all the intensity. For the other cases the two routes contributed comparably.

The final values for the quartet oscillator strength are also given in Table 7. The lifetimes were calculated assuming equilibrium among the magnetic sublevels. Thus the emission is averaged over both forbidden and allowed states.

5. Comparison with Experiment

A. Expected Decay Patterns

The above sections discuss the steady states of porphyrin complexes as coupled by exchange integrals, vibronic terms and spin-orbit effects. For luminescence decay patterns, it is necessary to use these states to predict radiationless decay rates as well as radiative decay. Unfortunately calculation of radiation less decay is not possible. It can be shown [7], using the theory of Lin [25], that singdoublet to tripdoublet radiationless decay will depend on exchange terms in a similar manner to the dependence of singlet to triplet decay on spin-orbit terms. Since the exchange terms are much larger, we can understand the absence of fluorescence as due to fast singdoublet to tripdoublet radiationless decay. It can also be shown that tripdoublet to quartet radiationless decay depends on terms similar to those coupling singlets to triplets and decay rates of 10^8/sec might be possible.

The simplest model that might be proposed for luminescence from the tripdoublet-quartet manifold would assume (1) that every photon absorbed produces an excitation to the tripdoublet, (2) that relaxation between the tripdoublet and quartet ($m_S = \pm 1/2$) is fast compared to luminescence decay, and (3) that the quartet ($m_S = \pm 3/2$) does not participate in the decay. Thus the population ratio of tripdoublet to quartet will be $D:Q = e^{-\Delta}:1$, where $\Delta = (E_D - E_Q)/kT$. Let k_f, k_p be the rates at which D, Q emit photons and k_f^*, k_p^* be the rates (radiative plus radiationless) at which D, Q decay to the ground state (see Fig. 3).

Then it is easy enough to derive the following equations:

$$\begin{aligned} \tau^{-1} &= (k_f^* e^{-\Delta} + k_p^*)/(1 + e^{-\Delta}), \\ \phi_D &= k_f e^{-\Delta}/(k_f^* e^{-\Delta} + k_p^*), \\ \phi_Q &= k_p/(k_f^* e^{-\Delta} + k_p^*), \end{aligned} \tag{37}$$

where τ is the luminescence lifetime of the tripdoublet-quartet system, ϕ_D is the quantum yield of tripdoublet luminescence, and ϕ_Q is the quantum yield of quartet.

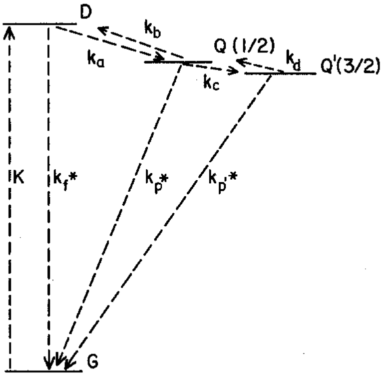

Fig. 3. Energy level diagram showing lowest tripdoublet and quartet levels and indicating decay pathways

There are five parameters in Eqs. (37). To give qualitative insight into the behavior of lifetime and quantum yields with temperature, we have plotted τ, ϕ_D, and ϕ_Q in Fig. 4 as a function of Δ assuming $k_f = k_f^* = 30 k_p^* = 100 k_p$, values that correspond roughly to the observations on CuOAP. We see that the yield of tripdoublet ϕ_D declines as temperature drops, while the yield of quartet ϕ_Q and the observed lifetime τ rises.

B. Experimental Observations

We have been carrying out in our laboratory a number of studies on the luminescence of VO, Co, and Cu complexes of porphyrins. So far an extensive account of the luminescence of CuOAP, CuTPP, and CuP (porphin) at liquid nitrogen temperature has been published [1f]. A preliminary account of the lumi-

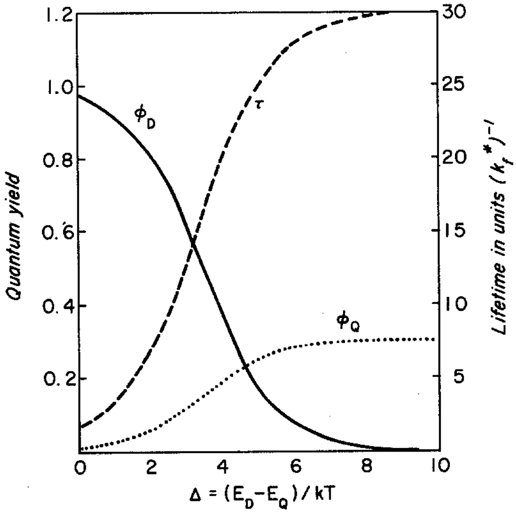

Fig. 4. Doublet and quartet quantum yields and luminescence decay time according to Eqs. (37) assuming $k_f = k_f^* = 30 k_p^* = 100 k_p$ (see text)

nescence of these same compounds in polymethylmethacrylate (PMM) in the temperature range 80° K to 10° K has appeared [25]. Other studies on Cu deuteroporphyrin, Cu 2,4-diacetyldeuteroporphyrin, Cu protoporphyrin, VO etioporphyrin, and VOTPP in PMM in the temperature range 300° K to 10° K have been carried out but are not fully analyzed [26]. Although luminescence from Co porphyrin has been reported [15] work in our own laboratory could not confirm it.

The most extensive studies were on a series of CuOAP complexes. We find that the luminescence yield is strongly temperature dependent increasing by a factor of ≈ 6 over the temperature range 300° K to 80° K. At 80° K the spectrum consists of a main peak with $\lambda \approx 690$ mμ with much weaker peaks from 720–770 mμ [1f]. A luminescence excitation spectrum establishes that $f \approx 10^{-4}$, $\varepsilon \approx 80$ liters/mole cm, $\tau_{\mathrm{nat}} \approx 70$ μsec. This compares quite satisfactorily with the calculated numbers given in Table 5. Experimental lifetimes in the temperature range 75° K–90° K vary from 60 μsec to 95 μsec. The measured quantum yield is ≈ 0.6. Thus there is little doubt that this luminescence is from the tripdoublet.

Our studies in PMM show that below 60° K there are striking changes in the spectrum, the luminescence yield, and the time decay [25, 26]. At 60° K, although the spectrum and the yield show little difference from that at 80° K, the luminescence decay is non-exponential. It can be described as a sum of two exponential decays, i.e. a "double lifetime" of 65/200 μsec. By 40° K the main luminescence peak at 690 mμ has decreased by about 1/3 and the double lifetime 155/1200 μsec is observed. The spectrum continues to change but the luminescence time decay is more stable. By 20° K the luminescence yield has fallen by a factor of 3 from that at 50° K and the spectrum is altogether different. There are peaks at 696 and 715 mμ of comparable intensity. The double lifetime is now 140/1400 μsec. At 10° K the two peaks are at 698 and 713 mμ with the second somewhat higher than the first. The double lifetime is 115/1250 μsec. Although the manner by which the 60° K spectrum changes to that at 10° K needs explanation, in the light of the theory developed in this paper it seems reasonable to interpret the low temperature luminescence as coming from the quartet state. From $\Delta\lambda \approx 8$ mμ we can estimate that $\Delta E_{DQ} \approx 170\ \mathrm{cm}^{-1}$, which compares to the calculated value $319\ \mathrm{cm}^{-1}$ given in Table 4. Our first analysis of the luminescence from the Cu complexes of deuteroporphyrin, 2-4-diacetyldeuteroporphyrin, and protoporphyrin shows qualitatively similar behaviour [26]. The results can be sharply contrasted with a similar study carried out on Zn etioporphyrin in PMM, which showed little variation in yield, spectrum, or lifetime between 80° K and 10° K [25].

Our results for CuTPP are strikingly different from those for CuOAP, yet can be understood by the theory developed above. The luminescence spectrum shows a single broad peak centered at $\lambda \approx 750$ mμ, which more resembles the CuOAP luminescence from the quartet than that from the tripdoublet. No mirror image luminescence excitation could be seen, but weak absorption peaks can be seen at 670 mμ and 713 mμ [1f]. These might be due to tripdoublet absorption. The luminescence decay at liquid nitrogen temperature is non-exponential, but can be analyzed as a "triple lifetime" of 25/145/610 μsec [1f]. The luminescence spectrum changes little with temperature. The luminescence decay does change and at 25° K seems largely exponential with a single lifetime ≈ 1140 μsec. The data then is quite consistent with the theoretical prediction that ΔE_{DQ} in CuTPP is about twice that of CuOAP so that at 80° K the luminescence comes from the quartet.

CuP behaves in an intermediate fashion between CuOAP and CuTPP. The spectrum is rather strongly temperature dependent in the range of $T \approx 80°$ K. Although the $0-0$ peak is strong, it does not dominate the spectrum as in CuOAP. At $T = 78°$ K the luminescence decay shows a double lifetime of 155/750 μsec [1f]. At 25° K the origin of the spectrum is red shifted $\approx 500\ \mathrm{cm}^{-1}$, and the decay is exponential with single lifetime of 1870 μsec [27]. It would seem then that ΔE_{DQ} in CuP is intermediate between CuTPP and CuOAP so that the change between doublet and quartet luminescence occurs in the 80° K temperature region. The results of a calculation on CuP have been included in Table 4. We see that CuP is predicted to behave like either CuTPP or CuOAP depending on whether the singdoublet $(a_{1u}e_g)$ or $(a_{2u}e_g)$ is assumed to be lower. The fact that the observed CuP luminescence is to the blue of that in CuOAP suggests that $(a_{1u}e_g)$ is lower. Hence $K(\sigma, \pi)$ in Matrix (12) may be dependent on substituents, a possibility not as yet allowed for in our calculations.

VO etioporphyrin (Etio), an octalkylporphin, has also been studied in PMM and is different from the Cu complexes [26]. From room temperature to 80° K the yield increases by a factor of ≈ 2.5, but there is no great change at lower temperature. The luminescence spectrum consists of a clear main peak at $\lambda \approx 710$ mμ with a tail extending about 50 mμ to the red. There is no marked change in the spectrum from room temperature down to our lowest measurements at 10° K. There is, however, a marked change in the luminescence decay. The decay shows a single lifetime of 90 μsec at 78° K and of 103 μsec at 58° K. However, at 36° K we find the double lifetime 30/160 μsec, at 21° K we find 50/350 μsec, and at 10° K we find 280/1450 μsec [26].

VOTPP has a luminescence spectrum in PMM that peaks at $\lambda \approx 745$ mμ and resembles CuTPP in being broad and structureless. However, unlike CuTPP, VOTPP gave us no long lived decay. At liquid nitrogen temperature a lifetime of about 20 μsec could be observed. But this appeared to decrease to about 10 μsec at liquid hydrogen temperature. No great change in the spectrum was observed [26]. Table 4 predicts that ΔE_{DQ} should be considerably larger for VOTPP than for VOEtio so that we expect long lived luminescence from the quartet. These VOTPP experiments then are at present inexplicable.

Table 7 contains predictions of triplet and quartet radiative lifetimes. At the present time we have little idea of the pathway for radiationless decay. For example, in ZnEtio porphyrin we know that $\phi_F \approx \phi_P \approx 0.04$ and that $\tau_P^* \approx 100$ msec [1g], where ϕ_F and ϕ_P are the quantum yields of fluorescence and phosphorescence and τ_P^* is the observed phosphorescence decay time. Depending on whether radiationless decay is $S_1 \rightarrow S_0$ or $T_1 \rightarrow S_0$, we can say that

$$(1-\phi_F)\,\tau_P^*/\phi_P > \tau_P > \tau_P^* \tag{38}$$

where τ_P is the radiative time. Thus for ZnEtio we find $2.4\ \mathrm{sec} > \tau_P > 0.1$ sec. The calculated value of 3 sec in Table 7 is then possible if most radiationless decay is from the triplet. Again for CuTPP, the low temperature luminescence lifetime gives $\tau_P^* \approx 1$ msec [25]; yields at liquid nitrogen temperature are $\phi_P \approx 0.06$ [1f]. If we assume the observed luminescence is from the quartet, we obtain as limits on the quartet lifetime 17 msec $> \tau_p >$ 1 msec. This value is much shorter than the calculated value of 1 sec in Table 7. It would seem, then, that the theoretical estimate of spin-orbit coupling for the Cu complexes is too low.

C. *Summary Comparison*

We have summarized the most salient experimental facts in Table 8. These can be understood most simply if the series VOEtio, CuOAP, CuP, CuTPP represent increasing energy gap between tripdoublet and quartet. It can be seen in Fig. 4 that with decreasing temperature substantial change can occur in the luminescence time even though the spectrum remains unchanged. Thus we believe $E_D - E_Q$ is sufficiently small for VOEtio that at all temperatures examined the luminescence comes from the tripdoublet. However, the lifetime changes at low temperature. For CuOAP spectral changes are observed and lifetime changes occur at higher temperatures. For CuP the changes occur near nitrogen temperature, while for CuTPP we believe luminescence is from the quartet. While theory does predict that $E_D - E_Q$ will be smaller for CuOAP than for CuTPP, the small size for VOEtio is not predicted. However, the experiments definitely confirm the presence of both tripdoublet and quartet states as envisaged by our calculations.

However, there are two results of the experimental studies of Cu and VO porphyrin luminescence that cannot be accounted for by Eqs. (37): (1) The yield ϕ_D decreases greatly as T rises toward room temperature and (2) the luminescence decay at low temperature is non-exponential. A way to account for the first result is to assume that there is a pathway with an activation energy by which the tripdoublet can radiationlessly decay to the ground state. To account for the second result it is necessary to assume that some radiationless relaxation rate among the tripdoublet-quartet states becomes slow at low temperature compared to the observed luminescence time. Such non-exponential decay has been observed in pyrazine [27] and quinoxaline [28] triplets at very low temperature and is attributed to lack of spin relaxation.

Table 8. *Observed luminescence maxima and lifetimes*

$T \approx 80°$ K		$T \approx 10°$ K	ΔE_{DQ}
VOEtio	710 mμ–90 μsec	710 mμ–280/1450 μsec	($\lesssim$ 50 cm^{-1})[b]
CuOAP	690 mμ–80 μsec	698 mμ–115/1250 μsec	170 cm^{-1}
CuP	660 mμ–155/750 μsec	683 mμ–1870 μsec	500 cm^{-1}
CuTPP	750 mμ–25/145/610 μsec	750 mμ–1140 μsec[a]	($\gtrsim$ 700 cm^{-1})[b]

[a] For CuTPP observation is at $T \approx 25°$ K.

[b] Guestimate.

6. Summary

We have considered in this paper the effect of an unpaired d electron on the triplet state of porphyrin. The triplet becomes a tripdoublet and a quartet. We have calculated the intensity of the tripdoublet and the tripdoublet-quartet energy gap, which depend on d-π-exchange integrals. We find these integrals are overestimated, but by scaling them to match energy we can predict intensity. We predict that the ratio of 0 – 1 to 0 – 0 intensity should be larger in the quartet than in the tripdoublet. We predict that the electronic configuration of the lowest tripdoublet-quartet states and hence the energy gap will be dependent on the substituents of the porphyrin ring. We predict that the radiative lifetime of the quartet will be dependent on the metal.

Experimental study of the luminescence of a number of Cu porphyrin complexes and VO etioporphyrin shows a unique temperature dependence of quantum yield, spectrum, and decay lifetime as compared to Zn etioporphyrin, which lacks an unpaired electron. In CuOAP and CuP we have identified distinct luminescence spectra due to the tripdoublet and quartet. In CuTPP the data suggests that the luminescence spectrum is due to the quartet, while in VOEtio it is due to the tripdoublet. Only the luminescence of VOTPP is not explained. A theoretical estimate of triplet radiative lifetime for ZnEtio is in accord with the data as is the theoretical prediction that the lifetime of the VO and Cu quartets will be shorter. However, the present theoretical estimate for the Cu porphyrin quartet lifetime seems too long compared to the data.

Finally we might point out that the experimental data gathered for the purpose of learning about the tripdoublet and quartet states have disclosed the existence of a complicated radiationless decay pattern. The experimental and theoretical investigation of this decay remains for the future.

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Appendix 1 — Variation of Parameters

It is important with any semi-empirical theory to see how sensitive final results are to small parameter variations. The critical parameters for the central metal in an EH model are: ζ_{3d} the metal $3d$ orbital exponent; κ, the EH interaction parameter; and α_s, α_p, α_d the metal one electron energies. The effect of variation of these parameters was systematically considered for the Cu complex. The results

Table 9. *Effect on exchange integrals of parameter variation*

Parameter	σ-π			π-π		
	$K(a_{1u}, b_{1g})$	$K(a_{2u}, b_{1g})$	$K(e_g, b_{1g})$	$K(a_{1u}, e_g)$	$K(a_{2u}, e_g)$	$(a_{1u}e_{gx}\|e_{gy}a_{2u})$
Normal[a]	37	569	351	6015	7660	5389
$\zeta_{3d}=2.5$	21	587	442	5932	7676	5366
$\zeta_{3d}=4.0$	60	584	344	6035	7687	5390
$\kappa=1.84$	31	658	366	6011	7641	5297
$\kappa=1.94$	26	609	359	5942	7678	5314
$\alpha_s=-6.78; \alpha_p=-2.18; \alpha_d=-9.65$	28	687	372	5904	7791	5289
$\alpha_s=-8.72; \alpha_p=-4.73; \alpha_d=-11.55$	29	618	367	5949	7684	5334

[a] $\zeta_{3d}=3.08$, $\kappa=1.89$, $\alpha_s=-7.75$, $\alpha_p=-3.95$, $\alpha_d=-10.60$.

are summarized in Table 9, where we report the resulting exchange integrals. The σ-π-exchange integrals include only one center terms and were not scaled.

It can be seen from Table 9 that the key integrals for tripdoublet intensity are not grossly affected by these parameter variations. For all these calculations the total range in radiative lifetime for $^2T(a_{2u}e_g)$ was 2.8 μsec to 18 μsec with the normal parameters giving 10 μsec while for $^2T(a_{1u}e_g)$, the range was 12 to 26 μsec with a normal value of 20 μsec. (These short lifetimes, compared to Table 5, are due to lack of scaling.) There was a 20% variation found for the doublet-quartet energy gap. Details of these and other comparisons are given elsewhere [7].

Appendix 2 — Pyridine Complex

Metal porphyrins are known to form pyridine complexes. It is known that the pyridine complex with CuTPP at room temperature [29] forms with a small equilibrium constant which shifts toward the complex at low temperature.

EH calculations were performed assuming the pyridine nitrogen was 2 Å above the Cu atom. The pyridine ring was positioned perpendicular to the porphyrin ring with the plane of the pyridine ring passing through two of the porphyrin ring nitrogens.Two geometries were taken: Case 1 in which the copper atom is in the plane of the porphyrin molecule; Case 2 in which the copper and the pyridine are moved as a unit perpendicularly to the porphyrin plane until the copper atom is 0.5 Å out of the plane of the porphyrin molecule, the location of the porphyrin atoms remaining fixed. The copper-pyridine distance is a common one in pyridinate complexes [30].

These calculations show rather strong mixing among the pyridine n orbital, the Cu d_{z^2} orbital, and the porphin $a_{2u}(\pi)$. This is rather different from the Ni-porphyrin pyridinate, where the orbitals remain relatively pure. This mixing predicts a very curious visible absorption spectrum and so the effect on the tripdoublet was not investigated.

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Dr. Robert L. Ake
Chemistry Department
Old Dominion University
Norfolk, Virginia, USA