Title
ZSEMAN EFFECT IN PORPHYRINS: ZERO-FIELD SPLITTING OF THE EXCITED ELECTRONIC STATES

Permalink
https://escholarship.org/uc/item/29s2f80m

Authors
Sutherland, J.C.
Axelrod, Daniel
Klein, M.P.

Publication Date
1970-11-01

Submitted to Journal of Chemical Physics

UCRL-20175
Preprint

c.2

ZEEMAN EFFECT IN PORPHYRINS: ZERO-FIELD SPLITTING OF THE EXCITED ELECTRONIC STATES

P.

J. C. Sutherland, Daniel Axelrod and M. R. Klein

November 1970

AEC Contract No. W-7405-eng-48

UCRL-20175 c.2

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

DISCLAIMER

ZEEMAN EFFECT IN PORPHYRINS:
ZERO-FIELD SPLITTING OF THE EXCITED ELECTRONIC STATES*

J. C. Sutherland,+ Daniel Axelrod and M. P. Klein

Laboratory of Chemical Biodynamics
Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

---

*Research sponsored, in part, by the U. S. Atomic Energy Commission.

+Postdoctoral fellow of the National Institute of General Medical Sciences, National Institutes of Health (5-F02-GM42776-02).

ABSTRACT

Recent experimental studies have reported anomalous and contradictory results for the absorption of left and right polarized light (LCPL and RCPL) by zinc and magnesium coproporphyrins in the presence of a magnetic field: for both compounds, the absorption bands for right and left circularly polarized light have distinctly different shapes at room temperature; at 77°K unexplained shoulders appear in the absorption spectra for both polarizations for the magnesium but not for the zinc compound; the value of the angular momentum of the lowest energy excited state computed from the separation of the peaks of the LCPL and RCPL absorption bands differs from the value obtained from a magnetic circular dichroism (MCD) experiments by nearly 50%; no shape anomalies were observed in the MCD spectra. We derive a general solution for the mixing of two states by a magnetic field and show that all of the anomalous experimental data are explained if a) the presumably degenerate pair of excited states are split in zero field by an energy comparable to the Zeeman energy but less than the spectral band widths, and also b) the overlapping transitions have unequal intensities. Our results show that MCD should give better estimates of excited state angular momenta while the direct measurement of LCPL and RCPL is superior in detecting non-degeneracy.

INTRODUCTION

Malley[1] and Malley, Feher and Mauzerall[2] recently measured the Zeeman effect on the visible absorption bands of zinc and magnesium coproporphyrin. Their data for the absorption of right and left circularly polarized light (RCPL and LCPL) by transitions to the lowest excited states ($Q_{0\leftarrow0}$ band[3]) of zinc coproporphyrin I are shown in Fig. 1. These data show asymmetries between the LCPL and RCPL absorption curves which are not predicted by simple theory[3,4] and for which Malley _et al._[1,2] offered no explanation. In the presence of a magnetic field, the RCPL band shifts to lower energy, exhibits a higher peak intensity and is narrower than is the LCPL band. Significantly, the areas under the two curves are equal. This result was found for both isomers I and III of zinc coproporphyrin (see Fig. 2) in a variety of solvents at room temperature and at 77°K. At room temperature, the spectra of magnesium coproporphyrin I were similar to the data shown in Fig. 1. At 77°K however, shoulders appeared on both the LCPL and RCPL absorption bands, another result which was not explainable.[1,2]

Malley _et al._[1,2] calculated the angular momentum, M_z, of the lowest excited state from the separation between the peaks of the LCPL and RCPL absorption curves. At room temperature they found about 9 units of angular momentum for both isomers and both metals. This value is in excellent agreement with the predictions of simple free electron theory[3,4] but greater than the value calculated from molecular orbital theory by about a factor of 2.[5] At 77°K the value of M_z decreased to about 6.4 for the zinc compound but increased for the magnesium compound.

Dratz[6] has studied the $Q_{0\leftarrow 0}$ bands of metalloporphyrins using magnetic circular dichroism (MCD). This technique makes a direct measurement of the difference in absorption between left and right circularly polarized light induced by an external magnetic field. The asymmetries found in the Zeeman experiment are not apparent in Dratz's data, nor are they observed when the MCD is calculated from the LCPL and RCPL absorption curves.[1] Dratz calculated M_z by comparing the MCD with the derivative of the absorption spectrum measured in the absence of an applied magnetic field. Using the same sample of zinc - coproporphyrin III employed by Malley et al.,[1,2] Dratz found that M_z was 6.5 ± 0.5 at room temperature. Under the same conditions, the MCD curve deduced from the Zeeman experiment gave a value of 7.0, in excellent agreement with Dratz's results.[1] Thus, there appeared to be systematic differences between the two supposedly equivalent techniques.

The spectra of porphyrin molecules have been investigated both experimentally and theoretically in great detail because of the central role of these molecules in photosynthesis and energy metabolism. In addition to their importance in numerous biological systems, porphyrins are inherently interesting to the spectroscopist because they are among the largest and most complicated molecules to which the techniques of molecular orbital theory have been successfully applied. Thus, the unexplained features found in the Zeeman spectra and the contradiction between this technique and MCD have led to considerable discussion and concern.[1,2,6,7]

We have found that all of the anomalous features of Malley et al.'s data for the $Q_{0\leftarrow 0}$ band can be explained and the apparent discrepancies between the Zeeman effect and MCD resolved by introducing the hypothesis that the two components of the presumably degenerate excited state differ in both energy and intensity (in the absence of an applied magnetic field). We use a general formalism for the mixing of excited states by a magnetic field which in the appropriate limits reduces to the solutions found previously by other workers.[8] The contradictory results found from the Zeeman experiment and MCD are shown to follow from inherent differences between the quantities measured by the two methods. Our conclusions lead to fundamental questions concerning the symmetry of the porphyrin's excited states and the nature of their spectra.

THEORY

We wish to find the changes in the absorption of circularly polarized light induced by an external magnetic field. Our model is a molecule with two excited states whose transition dipoles are mutually perpendicular. No simplifying assumptions are placed on the relative energies of the two states. We find a general solution to the problem and show that it is correct in the special cases when the two excited states have the same energy and also when their energies are greatly different. Our solution leads to sum rules whose predictions may be compared directly with experimental data.

The visible spectrum of metallo-porphyrins consist of the intense B,[3] or Soret bands, near 400 nm, and the much weaker Q,[3] bands in the red. Both the Q and Soret bands contain two components and arise from transitions whose dipole moments lie in the plane of the molecules' ring system and are perpendicular to each other.[9] We designate the ground state as $|0\rangle$ and the two electronic excited states associated with the Q bands as $|x\rangle$ and $|y\rangle$. The directions of the transition dipoles for $|x\rangle \leftarrow |0\rangle$ and $|y\rangle \leftarrow |0\rangle$ define a right handed orthogonal coordinate system, xyz, fixed with respect to the molecule. The functions $|x\rangle$ and $|y\rangle$ are ortho-normalized eigenstates with the following properties:

$$\begin{aligned} \mathcal{H}_0|x\rangle &= E_x|x\rangle \quad , \qquad & \mathcal{H}_0|y\rangle &= E_y|y\rangle \quad , \\ L_z|x\rangle &= -iM_z\hbar|y\rangle \quad , \qquad & L_z|y\rangle &= iM_z\hbar|x\rangle \ . \end{aligned} \tag{1}$$

where $\mathcal{H}_0$ is the complete Hamiltonian for the molecule in the absence of a magnetic field, and L_z is the angular momentum operator for the direction perpendicular to the molecular plane.

In the presence of a magnetic field of intensity H_z parallel to the positive z axis the Hamiltonian of the system becomes

$$\mathcal{H} = \mathcal{H}_0 + \frac{\beta}{\hbar} H_z L_z$$

where β is the Bohr magneton. The states $|x\rangle$ and $|y\rangle$ are no longer eigenfunctions of $\mathcal{H}$. We seek new eigenfunctions $|i\rangle$ in the form of linear combinations of the unperturbed states;

$$|i\rangle = C_{ix}|x\rangle + C_{iy}|y\rangle \quad . \tag{2}$$

The coefficients C_{ix} and C_{iy} are determined from the variational principle[10] which requires

$$\frac{\partial E_i}{\partial C_{ix}} = 0 \quad , \quad \frac{\partial E_i}{\partial C_{iy}} = 0$$

where $E_i = \langle i|\mathcal{H}|i\rangle$. In addition, we require that $|i\rangle$ is normalized. When the expressions for $\mathcal{H}$ and $|i\rangle$ are substituted into the matrix element $\langle i|\mathcal{H}|i\rangle$ and the derivatives of the resulting expression with respect to C_{ix} and C_{iy} are equated to zero we obtain:

$$\begin{bmatrix} E_x - E_i \, , & i\beta H_z M_z \\ -i\beta H_z M_z \, , & E_y - E_i \end{bmatrix} \begin{bmatrix} C_{ix} \\ C_{iy} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad . \tag{3}$$

Non-trivial solutions exist if and only if the determinant of the matrix vanishes. The values of E_i which fulfill this condition are:

$$\begin{aligned} E_1 &= \frac{E_y+E_x}{2} - \left\{ \left[\frac{E_y-E_x}{2} \right]^2 + \left[\beta H_z M_z \right]^2 \right\}^{1/2} \\ E_2 &= \frac{E_y+E_x}{2} + \left\{ \left[\frac{E_y-E_x}{2} \right]^2 + \left[\beta H_z M_z \right]^2 \right\}^{1/2} \quad . \end{aligned} \tag{4}$$

These equations become clearer and more compact if we introduce 3 new variables:

$$E_o = \frac{E_y+E_x}{2} \quad , \quad \Delta E_N = \frac{E_y-E_x}{2} \quad \text{and}$$

$$\Delta E_T = \{ \Delta E_N^{\;2} + [\beta H_z M_z]^2 \}^{1/2} \quad . \tag{5}$$

E_o is the mean energy of states $|x\rangle$ and $|y\rangle$, ΔE_N is the natural splitting of $|y\rangle$ and $|x\rangle$ from E_o, and ΔE_T is the total splitting of the perturbed states $|1\rangle$ and $|2\rangle$ from E_o in the presence of a magnetic field. Using the new notation Eqns. 4 become

$$E_1 = E_o - \Delta E_T \quad \text{and} \quad E_2 = E_o + \Delta E_T \quad .$$

The difference in energy between states $|1\rangle$ and $|2\rangle$ is a non-linear function of H_z whenever $\Delta E_N \neq 0$. This effect is illustrated in Fig. 3.

To find the new wavefunctions for the magnetically perturbed excited states, $|1\rangle$ and $|2\rangle$, we substitute E_1 and E_2 into Eqn. 3. After some manipulation[11] we get:

$$|1\rangle = \alpha|x\rangle + i\gamma|y\rangle \quad , \quad |2\rangle = \gamma|x\rangle - i\alpha|y\rangle \tag{6}$$

where

$$\alpha = \frac{\Delta E_T+\Delta E_N}{\{[\Delta E_T+\Delta E_N]^2 + [\beta H_z M_z]^2\}^{1/2}} \quad , \quad = \frac{\beta H_z M_z}{\{[\Delta E_T+\Delta E_N]^2 + [\beta H_z M_z]^2\}^{1/2}}$$

The coefficients α and γ are not independent, since $\gamma = \{1-\alpha^2\}^{1/2}$.

In the two limits of 1) complete degeneracy ($\Delta E_N = 0$) and 2) well resolved non-degeneracy ($\Delta E_N >> \beta H_z M_z$), Eqns. 6 reduce to the forms found by degenerate and first order nondegenerate perturbation theory. In the degenerate situation both α

and γ become $1/\sqrt{2}$ and

$$E_1 = E_o - \beta H_z M_z \quad , \qquad E_2 = E_o + \beta H_z M_z$$

$$|1> = \frac{|x> + i|y>}{\sqrt{2}} \quad , \qquad |2> = \frac{|x> - i|y>}{\sqrt{2}} \tag{6a}$$

while to first order in the non-degenerate limits we obtain

$$E_1 = E_x \quad , \qquad E_2 = E_y$$

$$|1> = |x> + \frac{i\beta H_z M_z}{E_y - E_x} |y> \tag{6b}$$

$$|2> = -i|y> + \frac{\beta H_z M_z}{E_y - E_x} |x> \; .$$

Next we calculate the transition probabilities for the absorption of left and right (LCPL and RCPL) traveling in the positive z direction. The dipole moments for these transitions are of the form $e<o|\underline{r}|i>$, where $\underline{r}$ is the radius vector in the xyz coordinate system (i.e., $\underline{r} = x\hat{x}+y\hat{y}+z\hat{z}$ where $\hat{x}$ is the unit vector along x, etc.), e is the charge on the electron and $|i>$ is given by Eqn. 2.

Since the transition dipoles $<o|\underline{r}|x>$ and $<o|\underline{r}|y>$ lie along the x and y axes respectively, terms like $<o|y|x>\hat{x}$, $<o|z|y>\hat{y}$, etc., vanish. Therefore, the transition dipole for $|i>\leftarrow|o>$ is

$$e<o|\underline{r}|i> \;=\; \hat{x}eC_{ix}<o|x|x> + \hat{y}eC_{iy}<o|y|y> \quad . \tag{7}$$

The probability of absorption of left and right circularly polarized light is given by:

$$R^2_{\substack{L\\R},i} = \left| \left(\frac{\hat{x}\pm i\hat{y}}{\sqrt{2}}\right) \cdot e\langle o|\underline{r}|i\rangle \right|^2 \qquad (8)$$

where $\frac{\hat{x}\pm i\hat{y}}{\sqrt{2}}$ are the unit vectors in the direction of the vector potentials for LCPL and RCPL evaluated at the origin of xyz. The plus sign is for LCPL and the minus sign is for RCPL.[12] By analogy, we define $R_x = e\langle o|x|x\rangle$ and $R_y = e\langle o|y|y\rangle$. Substitution of the expression for $e\langle o|\underline{r}|i\rangle$ given by Eqn. 7 into Eqn. 8 gives

$$R^2_{\substack{L\\R},i} = \left| \frac{C_{ix}R_x}{\sqrt{2}} \pm i\,\frac{C_{iy}R_y}{\sqrt{2}} \right|^2 .$$

Expressed in terms of the coefficients α and $\pm i\gamma$ defined by Eqns. 6, this becomes:

$$R^2_{L,1} = \frac{\alpha^2 R_x{}^2}{2} + \frac{\gamma^2 R_y{}^2}{2} - \alpha\gamma R_x R_y \ ,$$

$$R^2_{R,1} = \frac{\alpha^2 R_x{}^2}{2} + \frac{\gamma^2 R_y{}^2}{2} + \alpha\gamma R_x R_y \ ,$$

$$R^2_{L,2} = \frac{\gamma^2 R_x{}^2}{2} + \frac{\alpha^2 R_y{}^2}{2} + \alpha\gamma R_x R_y \ , \qquad (9)$$

and

$$R^2_{R,2} = \frac{\gamma^2 R_x{}^2}{2} + \frac{\alpha^2 R_y{}^2}{2} - \alpha\gamma R_x R_y \ .$$

Equations 9 give important sum rules for both the Zeeman effect and MCD. Recalling that $\alpha^2+\gamma^2 = 1$ we have

$$R^2_{L,1} + R^2_{L,2} = R^2_{R,1} + R^2_{R,2} = \frac{R_x{}^2 + R_y{}^2}{2} .$$

That is, the total absorption of LCPL measured in the Zeeman experiment is equal to the total absorption of RCPL and both are exactly one half the absorption intensity measured with unpolarized light (with or without a magnetic field). This result is valid whether or not R_x^2 and R_y^2 are equal.

MCD is the difference between the absorption of LCPL and RCPL. Thus Eqns. 9 show that the MCD of band 1 is equal in magnitude but opposite in sign to that for band 2 since

$$R^2_{L,2} - R^2_{R,2} = -(R^2_{L,1} - R_{R,1}) = 2\alpha\gamma R_x R_y \quad .$$

This result has been found previously for both special cases $\Delta E_N = 0$ and $\Delta E_N >> \beta H_z M_z$.[6]

In Results and Discussion we show that the differences in shape of the LCPL and RCPL absorption bands reported by Malley _et_ _al_.[1,2] are explained if we assume $\alpha \neq \gamma$ (_i.e._, $\Delta E_N \neq 0$) and $R_x^2 \neq R_y^2$.

CALCULATIONS

Thus far we have considered only molecules whose transition dipoles are perpendicular to the direction of propagation of the light they are absorbing. In order to compare our results with experimental data we must account for the random orientation and the spectral width of absorption bands of molecules in solution.

The coordinate system xyz of a single molecule described above is related to the laboratory coordinate system XYZ by Euler's angles θ, ϕ and ψ as shown in Fig. 4. The Poynting vector of the light beam and the magnetic field vector, $\underline{H}$, are both parallel to the positive Z axis. Since the molecules are randomly oriented in solution,[13] we calculate the absorption of circularly polarized light in xyz , by averaging the absorptions over all values of θ, ϕ and ψ. The probabilities of absorption of LCPL and RCPL by a molecule whose orientations with respect to XYZ is given by θ, ϕ and ψ is proportional to:

$$R^2_{\substack{L\\R},i}\,(\theta,\phi,\psi) \;=\; \left|\, e\left(\frac{\hat{X}\pm i\hat{Y}}{\sqrt{2}}\right)\cdot \langle o|\underline{r}|i\rangle \,\right|^2$$

where $\hat{X}$ and $\hat{Y}$ are unit vectors along the X and Y axes in the laboratory coordinate system and $\underline{r}$ is still the radius vector in the molecules coordinate system. When $\langle o|\underline{r}|i\rangle$ is replaced by the expression given in Eqn. 7 we find:

$$\begin{aligned} R^2_{\substack{L\\R},1}\,(\theta,\phi,\psi) &= \tfrac{1}{2}\left|\, B_{11}\alpha R_x \mp B_{22}\gamma R_y + iB_{12}\gamma R_y \pm iB_{21}\alpha R_x \,\right|^2 \\ R^2_{\substack{L\\R},2}\,(\theta,\phi,\psi) &= \tfrac{1}{2}\left|\, B_{11}\gamma R_x \pm B_{22}\alpha R_y - iB_{12}\alpha R_y \pm iB_{21}\gamma R_x \,\right|^2 \end{aligned} \qquad (10)$$

where

$$\begin{aligned} B_{11} &= \cos\psi\,\cos\phi - \cos\theta\,\sin\phi\,\sin\psi \\ B_{21} &= \cos\psi\,\sin\phi + \cos\theta\,\cos\phi\,\sin\psi \\ B_{12} &= -\sin\psi\,\cos\phi - \cos\theta\,\sin\phi\,\cos\psi \\ B_{22} &= -\sin\psi\,\sin\phi + \cos\theta\,\cos\phi\,\cos\psi \;. \end{aligned}$$

The component of the magnetic field intensity along the molecule's z axis is $H_z = H\cos\theta$. From Eqns. 6 and 4 we see that the coefficients α and γ and also the excited state energies are complicated functions of θ.

Before we average the transition probabilities over all orientations we must take account of the spectral broadening of a single electronic transition in solution. We choose Gaussian shape functions of unit area which have the form

$$\frac{1}{\Delta\sqrt{\pi}} \exp\left[\frac{\bar{\nu}-\bar{\nu}_i(\theta)}{\Delta}\right]^2$$

where $\bar{\nu} = E/hc$ is the wave number of the absorbed light, $\bar{\nu}_i = \frac{E_i}{hc}$ is the wave number of the bands maximum, E_i is the energy of the state and Δ is the band's width factor expressed in wave numbers.[14] The dimensions of $\bar{\nu}$, $\bar{\nu}_i$ and Δ are cm^{-1}.(Wave number and energy are equivalent parameters. In discussing the theory we will use energy, while the experimental data and our calculations are expressed in wave numbers). When the magnetic field is turned on, the absorption envelope of each molecule shifts rigidly (i.e., its shape does not change) from its original position centered at E_x or E_y to its new position at E_1 or E_2. Each band is thus displaced by an energy of $\Delta E_T - \Delta E_N$. However, the extent of the band's displacement is not a linear function of H as shown by Eqns. 4. Since E_1 and E_2 are functions of $H_z = H\cos\theta$, the displacement of each molecule's absorption envelope is also a function of the molecule's orientation.

The fraction of the molecules within a small increment centered about θ,ϕ and ψ is $\frac{1}{8\pi^2}\sin\theta d\theta d\phi d\psi$. The expression for the absorption of LCPL and RCPL of wave number $\bar{\nu}$ by the transition $|i\rangle \leftarrow |o\rangle$ averaged over all orientations thus becomes:

$$R^2_{\substack{L\\R},i}(\bar{\nu}) = \frac{1}{8\pi^{5/2}\Delta} \int_\theta\int_\phi\int_\psi \left(\exp\left[\frac{\bar{\nu}-\bar{\nu}_i}{\Delta}\right]^2\right) R^2_{\substack{L\\R},i}(\theta,\phi,\psi)\sin\theta d\theta d\phi d\psi \qquad (11)$$

where the expressions

$$R^2_{\substack{L\\R},i}(\theta,\phi,\psi)$$

are given from Eqn. 10. The integrals over ϕ and ψ involve only simple products of sines and cosines and were evaluated analytically. The remaining integration over θ was performed numerically by a digital computer. The program required that numerical values be assigned to R_x, R_y, E_x, E_y, M_z, β, and H. For β we used a value of 9.273×10^{-24} J-m^2/Wb. Varying H is equivalent to varying M_z, since they always appear multiplied together.

The experimentally observed parameters are molar extinction coefficients which are related to absorption probabilities by

$$\varepsilon(\bar{\nu}) = \left(\frac{16\pi^2 e^2 N}{3n\hbar 10^3 \ln 10}\right) \bar{\nu} R^2(\nu) .$$

where N is Avogadro's number, e is the charge on the electron, n is the index of refraction of the medium and $\hbar$ is Planck's constant divided by 2π. The program which computed the absorption probabilities converted them to molar extinction coefficients. It also combined the components to give the extinction coefficients for left and right circularly polarized light and for the MCD:

$$\varepsilon_L(\bar{\nu}) = \varepsilon_{L,1}(\bar{\nu}) + \varepsilon_{L,2}(\bar{\nu}) ,$$
$$\varepsilon_R(\bar{\nu}) = \varepsilon_{R,1}(\bar{\nu}) + \varepsilon_{R,2}(\bar{\nu})$$
and
$$\Delta\varepsilon_M(\bar{\nu}) = \varepsilon_L(\bar{\nu}) - \varepsilon_R(\bar{\nu}) .$$

Both $\varepsilon_L(\bar{\nu})$, $\varepsilon_R(\bar{\nu})$, $\Delta\varepsilon_M(\bar{\nu})$ and any desired combination of the unobservable components ($\varepsilon_x(\bar{\nu})$, $\varepsilon_y(\bar{\nu})$, $\varepsilon_{L,1}(\nu)$, $\varepsilon_{L,2}(\bar{\nu})$, $\varepsilon_{R,1}(\bar{\nu})$ and $\varepsilon_{R,2}(\bar{\nu})$) were plotted on the same wave number scale.

RESULTS AND DISCUSSION

The asymmetric distribution of absorption intensity measured in LCPL and RCPL is a direct consequence of non-degeneracy ($E_x \neq E_y$) and unequal absorption intensity (${R_x}^2 \neq {R_y}^2$) (vide infra). After demonstrating the asymmetry for the simple system treated in the theoretical section we will add the complications of finite band width and random orientation and show that our theory can reproduce qualitatively all the features of the experimental data. The relative merits of the molecular Zeeman effect and MCD are then compared on the basis of their sensitivities to changes in the theoretical parameters. Finally, we discuss possible causes of the nondegeneracy in metallocoproporphyrin and suggest new experiments.

The meaning of Eqns. 9 is clearer if we replace ${R_x}^2$ and ${R_y}^2$ by two new parameters ${R_o}^2$ and ΔR^2 where

$${R_x}^2 = \frac{{R_o}^2}{2} + \Delta R^2 , \qquad {R_y}^2 = \frac{{R_o}^2}{2} - \Delta R^2 .$$

When these expressions are substituted into Eqns. 9 we get:

$$\begin{aligned}
R^2_{L,1} &= \frac{{R_o}^2}{4} + (\alpha^2 - \tfrac{1}{2})\,\Delta R^2 - \alpha\{1-\alpha^2\}^{1/2}\left\{\frac{{R_o}^4}{4} - \Delta R^4\right\}^{1/2} ,\\
R^2_{R,1} &= \frac{{R_o}^2}{4} + (\alpha^2 - \tfrac{1}{2})\,\Delta R^2 + \alpha\{1-\alpha^2\}^{1/2}\left\{\frac{{R_o}^4}{4} - \Delta R^4\right\}^{1/2} ,\\
R^2_{L,2} &= \frac{{R_o}^2}{4} - (\alpha^2 - \tfrac{1}{2})\,\Delta R^2 + \alpha\{1-\alpha^2\}^{1/2}\left\{\frac{{R_o}^4}{4} - \Delta R^4\right\}^{1/2} ,\\
R^2_{R,2} &= \frac{{R_o}^2}{4} - (\alpha^2 - \tfrac{1}{2})\,\Delta R^2 - \alpha\{1-\alpha^2\}^{1/2}\left\{\frac{{R_o}^4}{4} - \Delta R^4\right\}^{1/2} .
\end{aligned} \qquad (12)$$

The asymmetries in the absorption of left and right circularly polarized light can now be seen directly. We will start with the simplest case of complete degeneracy and then show the effects first of slight nondegeneracy and then of unequal absorption.

Complete degeneracy means that $E_x = E_y$ and $\alpha = 1/\sqrt{2}$ (Eqns. 6a). Also, since $|x\rangle$ and $|y\rangle$ are physically indistinguishable,

$$R_x^{\ 2} = R_y^{\ 2} = \frac{R_o^{\ 2}}{2} \quad \text{and} \quad \Delta R^2 = 0 \ .$$

Under these conditions Eqns. 12 become

$$R^2_{L,1} = 0$$

$$R^2_{R,1} = \frac{R_o^{\ 2}}{2}$$

$$R^2_{L,2} = \frac{R_o^{\ 2}}{2}$$

$$R^2_{R,2} = 0 \ .$$

These results are shown schematically as part I of Fig. 5. Transitions to state 1 absorb only RCPL and those to state 2 absorb only LCPL.

Next, we suppose that states $|x\rangle$ and $|y\rangle$ are slightly nondegenerate in energy but ΔR^2 is still equal to zero. In this case α is no longer equal to $1/\sqrt{2}$. However, the product $\alpha\{1-\alpha^2\}^{1/2}$ has a maximum value of 1/2 when $\alpha=1/\sqrt{2}$. Thus, the $\alpha\{1-\alpha^2\}^{1/2}$ terms in Eqns. 12 have absolute values less than $R_o^{\ 2}/4$. The result, shown as II in Fig. 5, is that an increment of intensity

$$\left(\frac{1}{2} - \alpha\{1-\alpha^2\}^{1/2} \right) \frac{R_o^{\,2}}{2}$$

is transferred from 1 to 2 in RCPL and from 2 to 1 in LCPL. However, this shift in intensity does not account for the asymmetries in the experimental data (Fig. 1) since the absorption in LCPL can be converted into that for RCPL by reflecting all components about E_o.

Finally, we note that if states 1 and 2 have different energies, they are distinguishable. Thus, there is no reason to require $R_x^{\,2} = R_y^{\,2}$. To illustrate the effect of unequal intensities, we take $R_x^{\,2} > R_y^{\,2}$ so $\Delta R^2 > 0$. Both the second and third terms of Eqns. 12 are affected. The presence of ΔR^4 in the third terms causes a transfer of intensity with the same symmetry as described above. We can think of this as an adjustment to the values obtained in going from I to II in Fig. 5. The asymmetry comes from the $(\alpha^2-1/2)\,\Delta R^2$ terms since they transfer intensity from state 2 to state 1 in both LCPL and RCPL. This effect is shown in part III of Fig. 5. The absorption is now asymmetric. In RCPL most of the intensity is located in the transition to state 1, while in LCPL it is divided more equally between the transitions to states 1 and 2.[15]

The asymmetries in LCPL and RCPL require that both the intensities and the energies of states $|x\rangle$ and $|y\rangle$ be unequal as is shown by considering the case where $E_x = E_y$ but $R_x^{\,2} \neq R_y^{\,2}$. The coefficient α depends on E_x and E_y but not on $R_x^{\,2}$ and $R_y^{\,2}$ and will be $1/\sqrt{2}$. Thus, $(\alpha^2-1/2)$ is equal to zero and the only effect is to transfer some intensity from 1 to 2 in RCPL and from 2 to 1 in LCPL resulting in a distribution pattern of type II as shown in Fig. 5.

Finally we consider randomly oriented molecules with absorption bands of finite width. The integral expressions for extinction coefficient as a function of wavelength were evaluated numerically as discussed above. Fig. 6 shows results which correspond to case III of Fig. 5. In RCPL, most of the absorption intensity is due to the transition to the lower energy states while in LCPL it is shared between both states. Thus the peak of the RCPL band is quite near the peak of its state 1 component while the peak of LCPL is broader and located between the state 1 and 2 components. The shapes of the RCPL and LCPL bands in Fig. 6 are strikingly similar to the experimental data of Fig. 1. The LCPL and RCPL absorption curves and MCD are complicated functions of $\beta M_z H$, ΔE_N, ΔR^2 and the width Δ.[16] The influence of each of these parameters was determined by computing the absorption of LCPL, RCPL and the MCD for a series of values. Particular attention was given to changes in position of the peaks of LCPL and RCPL absorption, since Malley et al.[1,2] used peak separation to calculate M_z. Figure 7 shows the effect of increasing ΔR^2. The total absorption intensity, R_0, is constant. The curve for RCPL narrows and the peak intensity increases as ΔR^2 becomes larger. The position of the RCPL peak moves slowly towards lower energy. The peak in LCPL drops and also moves to lower energies. Neither effect is linear in ΔR^2. The LCPL curve also becomes wider. Changes in ΔR^2 affect the MCD only slightly even in the most extreme case.

The wave number at which the MCD passes through zero is an isosbestic point. In the appendix, we show that this is a general result and that the crossing point corresponds to E_0, the mean energy of the two component states. Thus, E_0 is a physically measurable quantity and not merely a parameter in the theory.

Figure 8 shows the effect of increasing ΔE_N when $\Delta R^2 > 0$. Case A represents accidental degeneracy, i.e., $\Delta E_N = 0$, $\Delta R^2 \neq 0$. Increasing values of ΔE_N cause both the LCPL and RCPL curves to decrease in peak intensity and increase in width. However, both effects are weaker in RCPL so this curve becomes higher and more narrow relative to LCPL. In curve D, for which the natural splitting, $2\Delta E_N$, is one and one half times the width factor, Δ, both LCPL and RCPL have shoulders which mark the location of their "minor" components. The shoulders are located at positions under the peaks of absorption for the other polarization. The separation in peak position has increased greatly over that in case A. Case D thus corresponds closely to the experimental results found by Malley et al. for magnesium coproporphyrin I measured at 77°K. For both polarizations there occurred a shoulder virtually coincident with the wavelength of the peak observed in the other polarization. Values of excited state angular momenta calculated from the separation in the peaks of LCPL and RCPL were unrealistically high ($M_z > 10$).[1,2] The agreement between the low temperature spectra of magnesium coproporphyrin and curve D of Fig. 8 is convincing evidence that our model is correct.

One unusual feature of the data on magnesium coproporphyrin I in EPA is that at room temperature R_x^2 is greater than R_y^2, while at 77°K R_y^2 appears greater than R_x^2 (see Ref. 15). This may be related to the loss of about one-half of the intensity of both the LCPL and RCPL components when the sample is cooled from 300 to 77°K.

The data in Figs. 7 and 8 are calculated for a magnetic field of 10 Wb/m^2. We investigated the relationship between peak position and magnetic field by modifying our program to calculate automatically the position of the absorption maxima by interpolation. Figure 9 shows the position of the peaks in the absorption of LCPL and RCPL relative to the position of the absorption maximum at zero field[17] for values of H from 0 to 10 Wb/m^2. In Fig. 9A, R_x^2 and R_y^2 are equal. The peaks are split symmetrically (as are the entire absorption envelopes). However, the splitting is not a linear function of H for $\Delta E_N \neq 0$. Calculating M_z from the observed splitting would always give too large a result. Figures 9B and C show that when $\Delta R^2 \neq 0$, the splitting is no longer symmetric. In case B, the value of M_z calculated from the separation of the peaks will always be too large while in case C it will always be too small. Malley _et al._[1,2] measured the position of the peaks as a function of H for zinc coproporphyrin I in dioxane. However, their experimental uncertainty is too large to permit meaningful comparison with our calculations. The results of calculations in which the width of the absorption curve was varied showed that peak positions are relatively insensitive to this parameter as long as the state 1 and 2 components are unresolved.

Magnetic circular dichroism and the molecular Zeeman effect are complementary techniques. MCD depends only on the last term of Eqns. 12 while the Zeeman experiment depends on all of the terms in these equations. As a result the Zeeman effect is superior to MCD for detecting slight non-degeneracy (_i.e._, $\Delta E_N \neq 0$, $\Delta R^2 \neq 0$). Conversely, the magnitude of the separation between the peaks of the two Zeeman components gives unreliable estimates of M_z, as Figs. 7, 8 and 9 demonstrate. Figure 7 shows that the MCD is insensitive to changes in ΔR^2. The MCD is also insensitive to the natural splitting when ΔE_N is small compared to the width of the absorption band. Of the four cases presented in Fig. 8, the room temperature data on coproporphyrin are closest to curve B ($E_y - E_x = 50\ \text{cm}^{-1}$). This splitting produces less than a 5% change in the MCD. This insensitivity is a consequence of the form of the terms in Eqns. 12 which give rise to MCD. Suppose that introducing a non-zero value of ΔE_N causes α to become slightly larger than $1/\sqrt{2}$. Then $\{1-\alpha^2\}^{1/2}$ will be slightly less than $1/\sqrt{2}$, but the product, $\alpha\{1-\alpha^2\}^{1/2}$ will change less than either of its components. A similar argument holds for the product $R_x\ R_y$ and shows that MCD is also insensitive to changes in the relative intensities of transitions to $|x\rangle$ and $|y\rangle$.

As a test of the values of M_z calculated from MCD, we analyzed computed MCD and absorption spectra by a technique similar to that employed by Dratz.[6] For values of ΔE_N less than $\Delta/4$, the value of M_z recovered from the simulated experimental data were correct to within 10%. Thus, MCD should give relatively good estimates of M_z. Indeed, Dratz's[6] values of M_z for a variety of metalloporphyrins range from 4.4 to 6.5, and thus are close to the theoretical value of 4.35 predicted from MO theory by McHugh _et al_.[5]

If the aliphatic substituents are ignored, metallo-coproporphyrins have D_{4H} symmetry. Inclusion of the substituents reduces the symmetry of isomer I to C_{4H}. In this group, the representations of $|x\rangle$ and $|y\rangle$ remain degenerate. Isomer III belongs to group C_S, in which the degeneracy between $|x\rangle$ and $|y\rangle$ is formally removed. However, Malley et al.[1,2] observed the same asymmetry in the LCPL and RCPL absorption bands for both isomers I and III. Therefore, the substituents are probably not responsible for the lack of exact degeneracy which brings about the asymmetry of the absorption bands.

A clue to the origin of the effect may be found in changes in the Zeeman spectra produced by lowering the sample's temperature. For zinc - coproporphyrin III in EPA, reducing the sample's temperature from 300 to 77°K causes the value of M_z calculated from the separation of LCPL and RCPL absorption peaks to decrease from 8.6 ± 0.6 to 6.4 ± 0.6.[1,2] For magnesium coproporphyrin III, lowering the temperature reveals shoulders to the state 1 and state 2 components in LCPL and RCPL, respectively, suggesting that ΔE_N is larger in this molecule relative to the width of the absorption band. Three other changes occur when the temperature is reduced: 1) the $Q_{0\leftarrow0}$ band shifts to lower energy, 2) the absolute intensity of both polarization components decreases, and 3) the relative intensities of the absorption bands reverse (i.e., at 300°K, $R_x^2 > R_y^2$, while at 77°K $R_y^2 > R_x^2$). The $Q_{0\leftarrow0}$ band of the zinc compound shifts slightly to higher energy and the intensity effects are not observed. We have shown that changes in ΔE_N and ΔR^2 can alter the positions of the peaks in the LCPL and RCPL absorption curves. These parameters, therefore, may be functions of temperature. The physical basis for the removal of the degeneracy could involve either molecular vibrations or solute - solvent interactions.

Jahn and Teller showed[18] that the equilibrium configuration of the nuclei of a non-linear molecule in a totally symmetrical vibrational mode and a degenerate electronic state is always such as to relieve the degeneracy. For example, the highest symmetry possible for a porphyrin molecule, ignoring substituents, is D_{4H}. But the dependence of the electronic wavefunction on the nuclear coordinates will always cause the actual symmetry of the molecule to be no higher than D_{2H}. The observed temperature effects might be produced through changes in the dielectric constant of the medium. Perhaps molecular orbital calculations can predict if the observed zero-field splitting (of the order of 100 cm^{-1}) can be accounted for by "reasonable" nuclear distortions.

Another possibility is that the relatively weak $Q_{0\leftarrow 0}$ bands might gain intensity when the molecule is perturbed by random interactions with the solvent. Since a random perturbation is likely to be asymmetric, the spectrum would be heavily weighted by those molecules whose symmetry had been lowered. This hypothesis predicts that the LCPL and RCPL curves would be symmetric for the much stronger Soret band, where changes in intensity due to small distortions would be minor. Unfortunately, Malley et al. report that their experiment was insufficiently sensitive to detect any significant differences in the absorption of LCPL and RCPL by the Soret band. New experiments capable of detecting shape differences and splittings in the Soret band would be very useful. Measurements should also be made on other metal-porphyrins to determine if the effect is unique to coproporphyrin.

Our theory accounts qualitatively for all of the unusual effects observed by Malley et al.[1,2] for the $Q_{0\leftarrow 0}$ bands of zinc - and magnesium coproporphyrin. It also allows us to assess the relative merits of MCD and the Zeeman experiment. However, we raise a new and fundamental question: What is responsible for removing the degeneracy of the excited states of metallo-porphyrins? The answer to this question should represent a significant advance in our understanding of the electronic structure and spectroscopy of all porphyrins.

Appendix

If the natural splitting, $2\Delta E_N$, between the two unresolved components of a nearly degenerate absorption band is small compared to the spectral band width, we can derive an expression for the MCD for which the integration over θ can be performed analytically. We also show how, in principle, the parameters ΔE_N and ΔR^2 may be determined from experimental data.

The total absorption intensities for LCPL and RCPL are the sums of the intensities of the two component states; i.e.,

$$R^2_{\substack{L\\R}}(\bar{\nu}) = R^2_{\substack{L\\R},1}(\bar{\nu}) + R^2_{\substack{L\\R},2}(\bar{\nu}) \;. \tag{13}$$

The MCD is proportional to $R^2_L(\bar{\nu}) - R^2_R(\bar{\nu})$. We abbreviate this difference as $\delta R^2_M(\bar{\nu})$. From equation 13 we find

$$\delta R^2_M(\bar{\nu}) = \left(R^2_{L,1}(\bar{\nu}) - R^2_{R,1}(\bar{\nu})\right) + \left(R^2_{L,2}(\bar{\nu}) - R^2_{R,2}(\bar{\nu})\right) \;. \tag{14}$$

Each of the terms on the right side of equations 13 and 14 can be written in the form

$$R^2_{\substack{L\\R},i}(\bar{\nu}) = \frac{1}{8\pi^2}\iiint f(\bar{\nu},\bar{\nu}_i)\, R^2_{\substack{L\\R},i}(\theta,\phi,\psi)\,\sin\theta d\theta d\phi d\psi \;. \tag{15}$$

Equation 15 is identical to equation 11 except that the Gaussian band envelope has been replaced by a generalized shape function, $f(\bar{\nu},\bar{\nu}_i)$, which we assume to be of unit area. The shape of the envelope is the same for all the bands and the envelopes for components 1 and 2 have their maximum values at $\bar{\nu}_1$ and $\bar{\nu}_2$, respectively. When the magnetic field is turned on, the absorption envelope shifts rigidly from $\bar{\nu}_x$ to $\bar{\nu}_1$ or from $\bar{\nu}_y$ to $\bar{\nu}_2$.

We replace each term on the right of equation 14 by the corresponding form of equation 15, perform the integrations over ϕ and ψ and find

$$\delta R_M^2(\bar{\nu}) = R_x R_y \int_\theta [f(\bar{\nu},\bar{\nu}_2) - f(\bar{\nu},\bar{\nu}_1)] \, \alpha\gamma \cos\theta \sin\theta d\theta \qquad (16)$$

where the coefficients α and γ are still functions of θ. Since ΔE_T is small compared to the spectral band width, we expand $f(\bar{\nu},\bar{\nu}_i)$ around $\bar{\nu}_0$, ignore all terms above first order, and obtain

$$f(\bar{\nu},\bar{\nu}_i) = f(\bar{\nu},\bar{\nu}_0) \pm \Delta E_T \frac{df}{d\nu} (\bar{\nu},\bar{\nu}_0) \qquad (17)$$

where the + and - signs correspond to components 1 and 2. We also note from equation 6 that

$$\alpha\gamma = \frac{\beta M_z H \cos\theta}{2\Delta E_T} . \qquad (18)$$

Substitution of equations 17 and 18 into equation 16 results in an integrable expression, and we find

$$\delta R_M^2(\bar{\nu}) = -\frac{2}{3} R_x R_y \beta M_z H \frac{df(\bar{\nu},\bar{\nu}_0)}{d\bar{\nu}} . \qquad (19)$$

Equation 19 shows that, to this first order approximation, MCD is independent of ΔE_N. As we showed in Results and Discussions, the product R_xR_y varies only slightly with ΔR^2. Both of these results are apparent from the computer generated curves of Figs. 7 and 8. Equation 19 also shows that MCD passes through zero at $\bar{\nu}_0$,[19] the mean energy of the two unperturbed components of the zero-field total absorption band. This result is true to any order of approximation; if we extend the expansion of equation 17, all even order derivatives of $f(\bar{\nu},\bar{\nu}_0)$ cancel in the subsequent calculation. In principle, then, MCD can be used both to measure $\bar{\nu}_0$ and to detect non-degeneracy, since the value $\bar{\nu}_0$ deduced from the zero-crossing of MCD will differ from the location of the peak of the unperturbed absorption band if $\Delta E_N \neq 0$ and $\Delta R^2 \neq 0$. (The effects of non-degeneracy are more obvious in the Zeeman components, however.) Furthermore, the MCD has the shape of the derivative of either of the unperturbed near-degenerate components of the original absorption band, but the shape is not the derivative of the experimentally observed total absorption. Thus the MCD contains information about the shape of the individual components of the absorption band which cannot be obtained from total absorption or Zeeman spectra.

Equation 19 leads to a method for finding ΔE_N and ΔR^2 from the experimental MCD and absorption spectrum. The total absorption probability measured in the absence of a magnetic field is

$$R_0^2(\bar{\nu}) = R_x^2(\bar{\nu}) + R_y^2(\bar{\nu}) \qquad (20)$$

where

$$R_x^2(\bar{\nu}) = f(\bar{\nu},\bar{\nu}_x)\,\frac{R_x^2}{3}$$

and

$$R_y^2(\bar{\nu}) = f(\bar{\nu},\bar{\nu}_y)\,\frac{R_y^2}{3}\,. \qquad (21)$$

(Equations 21 can be deduced from equation 15. The integrals are easy to evaluate because in zero field the absorption probabilities are proportional to $\cos^2\theta$). We substitute equations 21 into equation 20, expand the absorption envelopes about $\bar{\nu}_0$ and find

$$R_0^2(\bar{\nu}) = \frac{1}{3}\,(R_x^2 + R_y^2)\, f(\bar{\nu},\bar{\nu}_0) + \frac{1}{3}\,\Delta E_N (R_x^2 - R_y^2)\, \frac{df}{d\bar{\nu}}\,(\bar{\nu},\bar{\nu}_0)\ . \qquad (22)$$

The second term on the right in equation 22 has the frequency dependence of $\frac{df}{d\bar{\nu}}\,(\bar{\nu},\bar{\nu}_0)$, which according to equation 19, is proportional to the MCD. The other term in equation 22 has the frequency dependence of $f(\bar{\nu},\bar{\nu}_0)$. The latter may also be expressed in terms of MCD since we can integrate equation 19 to give

$$f(\bar{\nu},\bar{\nu}_0) = \frac{-3}{2R_xR_y\beta M_zH} \int_0^{\bar{\nu}} \delta R_M^2(\bar{\nu}')\,d\bar{\nu}'\ . \qquad (23)$$

We substitute the values of $f(\bar{\nu},\bar{\nu}_0)$ and $\frac{df}{d\bar{\nu}}\,(\bar{\nu},\bar{\nu}_0)$ from equations 23 and 19 into equation 22 and find

$$R_0^2(\bar{\nu}) = A \int_0^{\bar{\nu}} \delta R_M^2(\bar{\nu}')\,d\bar{\nu}' + B\,\delta R_M^2(\bar{\nu}) \qquad (24)$$

where

$$A = -\left(\frac{R_y}{R_x} + \frac{R_x}{R_y}\right) \Big/\ 2\beta M_zH$$

and (25)

$$B = \Delta E_N\left(\frac{R_y}{R_x} - \frac{R_x}{R_y}\right) \Big/\ 2\beta M_zH\ .$$

We can find the coefficients A and B by resolving $R_0^2(\bar{\nu})$ as a sum of the experimental values of $\delta R_M^2(\bar{\nu})$ and $\int_0^{\bar{\nu}} \delta R_M^2(\bar{\nu}')\,d\bar{\nu}'$ by a least squares procedure. Once A and B are known, ΔE_N and ΔR^2 can be calculated from equations 25.

We analyzed computer generated data by the method outlined above and recovered the input value of ΔE_N to within ±25% and the input value of ΔR^2 to within ±15%. As expected, the analysis started to fail when the zero field splitting, $2\Delta E_N$, became greater than one half of the spectral bandwidth. This is not a serious limitation, because the method fails at about the point where the two components become resolved in the absorption spectrum, and this procedure is no longer necessary.

ACKNOWLEDGMENTS

We thank Professors K. Sauer and M. Calvin for helpful discussions.

FOOTNOTES AND REFERENCES

1. M. Malley, Ph.D. dissertation, University of California, San Diego, 1967.
2. M. Malley, G. Feher, and D. Mauzerall, J. Molecular Spectroscopy <u>26</u>, 320 (1968).
3. J. R. Platt, in <u>Radiation Biology</u>, edited by A. Hollaender (McGraw-Hill, New York, 1956), Vol. 3, p. 71.
4. W. T. Simpson, J. Chem. Phys. <u>17</u>, 1218 (1949).
5. A. J. McHugh, M. Gouterman, and C. Weiss, Jr., in preparation.
6. E. A. Dratz, Ph.D. dissertation, University of California, Berkeley, 1966.
7. Charles Weiss, Jr., J. Molecular Spectroscopy, In press.
8. See for example: A. D. Buckingham and P. J. Stevens, Ann. Rev. Phys. Chem. (1969), p. 399.
9. M. Gouterman, J. Molecular Spectroscopy <u>6</u>, 138 (1961).
10. See for example: Gerald W. King, in <u>Spectroscopy and Molecular Structure</u> (Holt, Rinehart and Winston, New York, 1965), p. 51.
11. In deriving Eqns. 6, we used the identity:

$$(\Delta E_T - \Delta E_N)\,(\Delta E_T + \Delta E_N) = [\beta H_z M_z]^2 \ .$$

12. According to this sign convention the tip of the electric vector of the incident LCPL traverses a right-handed helix. See: J. D. Jackson, in <u>Classical Electrodynamics</u> (John Wiley & Sons, New York, 1963), Chapter 7.

13. Malley[1] showed that orientation of the diamagnetic ground state molecules by the magnetic field is inconsequential even at 77°K compared to thermal randomization.

14. The broadening of an isolated absorption band of a molecule in solution is due to solute-solvent interactions and unresolved rotational structure. We assume that these effects are the same for the transitions to states $|1>$ and $|2>$. Thus, we use the same width factor for both bands.

    The experimental absorption bands cannot be fit exactly by one Gaussian function. The fit could be improved, for example, by multiplying the shape function by $(\bar{\nu}/\bar{\nu}_i)^n$ at the expense of introducing another parameter, n. Since our objective is a qualitative understanding of the data shown in Fig. 1, we omit this refinement.

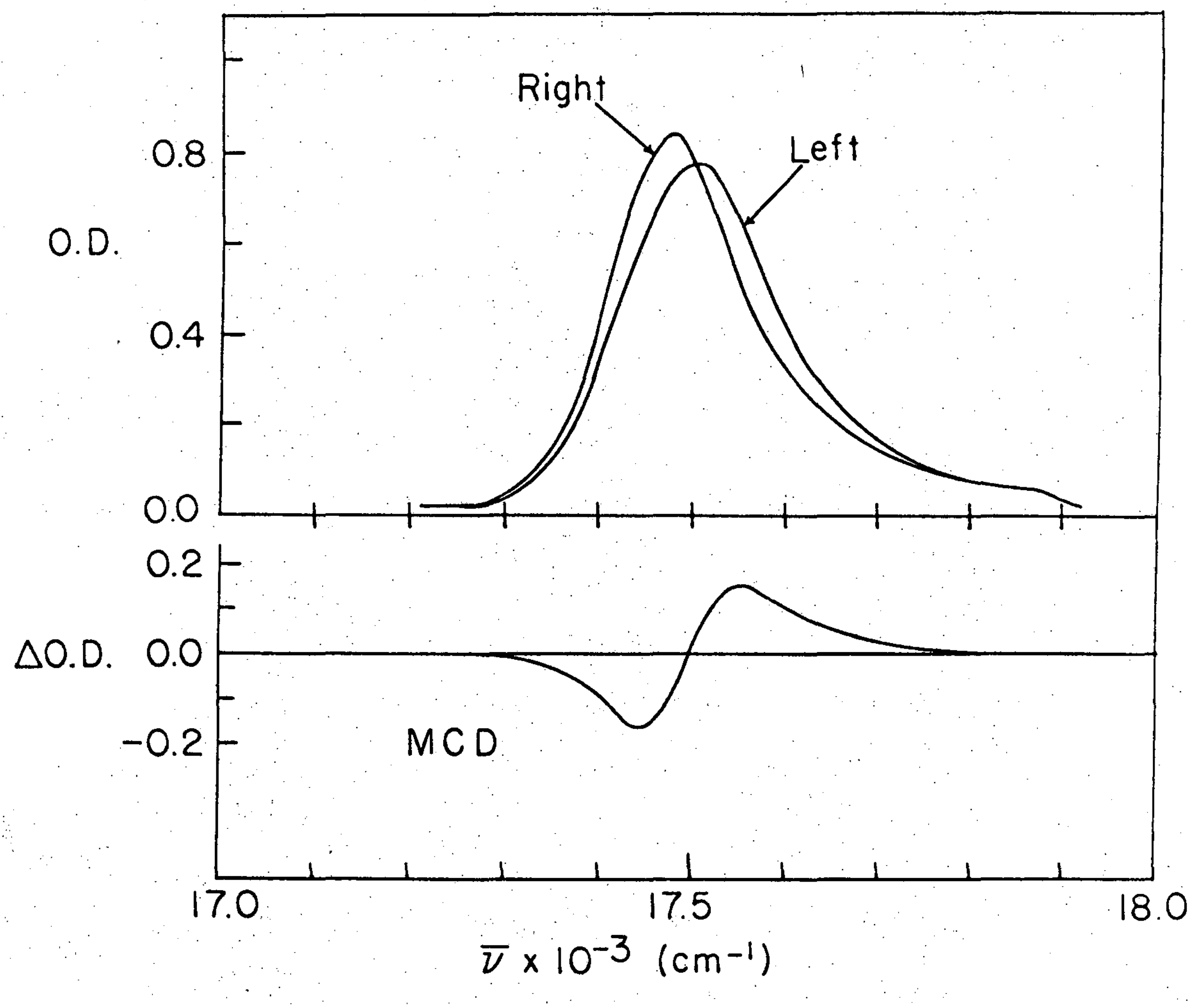
15. If R_x^2 is less than R_y^2 ($\Delta R^2<0$), the transfer of intensity is from 1 to 2 for both polarizations. The polarized absorption curves are still asymmetric, but now RCPL has the lower intensity at its peak and a broader shape. This situation is observed for magnesium coproporphyrin I at 77°K.[1]

16. The expression for the MCD (i.e., $\Delta\varepsilon_M$) can be simplified and the significance of the various parameters determined analytically if $\Delta E_T < \Delta/hc$. See the Appendix.

17. The shift in peak position caused by changes in ΔR^2 and ΔE_N in Figs. 7 and 8 are relative to an absolute wave number scale, while in Fig. 9 they are relative to the position of the absorption peak for $H = 0$. This peak has a different absolute position for different values of ΔR^2.

18. H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161, 220 (1937).

19. The magnetic field also mixes the nearly degenerate states being studied with other states of the same symmetry (e.g., the Soret band states in porphyrins), thus producing very small "B" terms in the MCD. This effect can be treated by nondegenerate perturbation theory.



XBL 709-5422

Fig. 1. The absorption of LCPL and of RCPL as a function of wave number in the $Q_{0,0}$ band of zinc coproporphyrin I in a magnetic field of 10 Wb/m^2. The magnetic circular dichroism is the difference between the LCPL and RCPL absorption curves. The sample was dissolved in EPA and cooled to 77°K. The data were taken from Ref. 2.

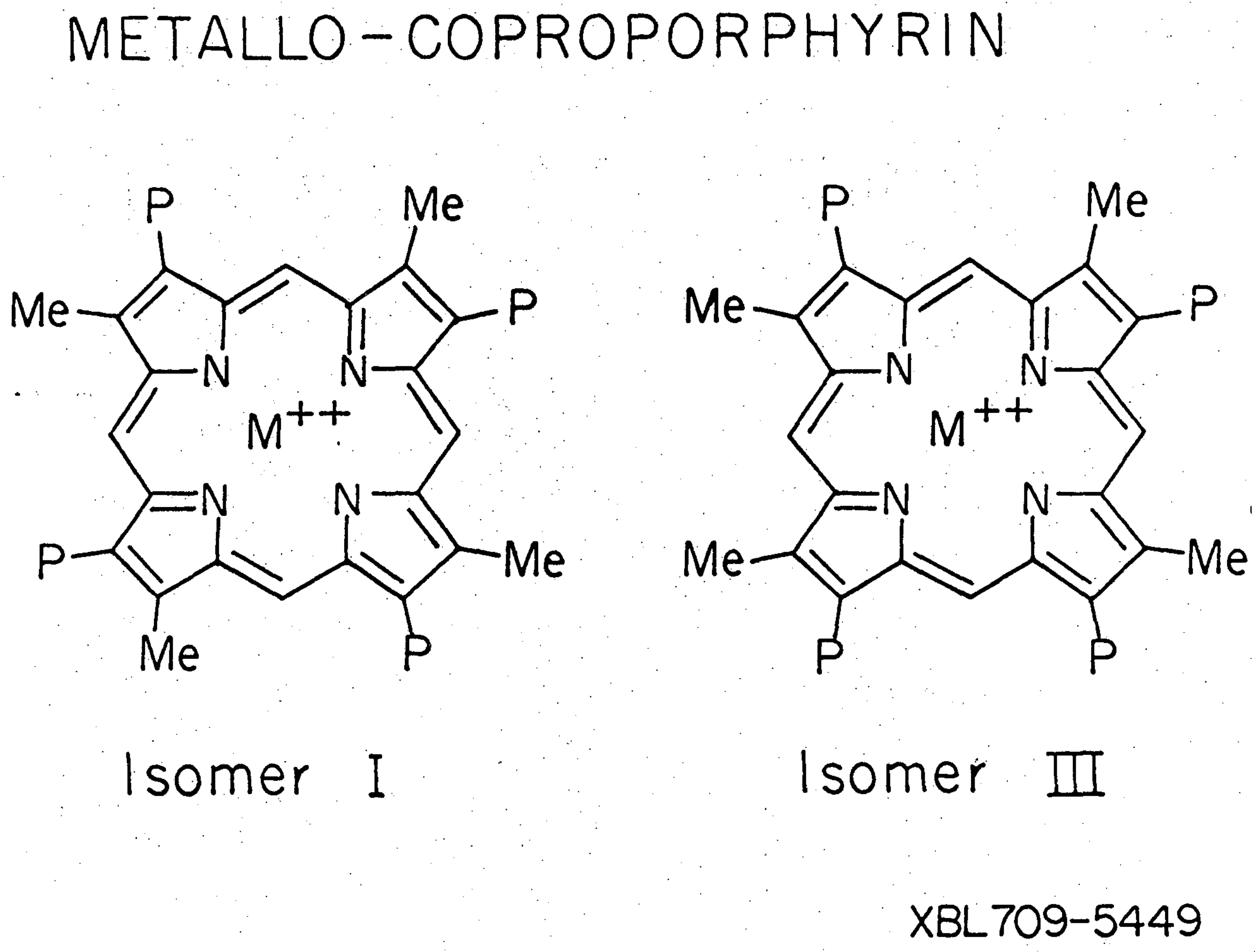
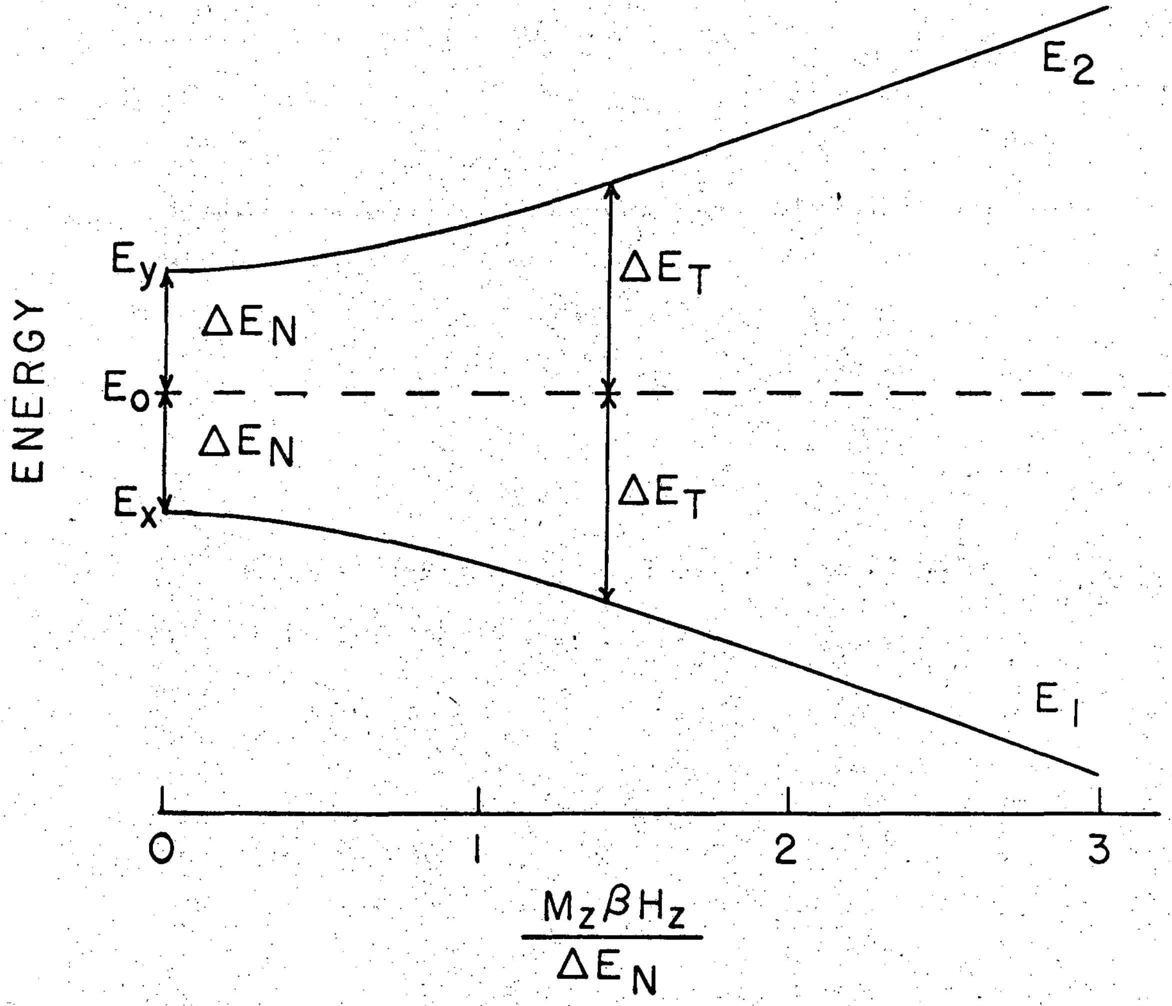
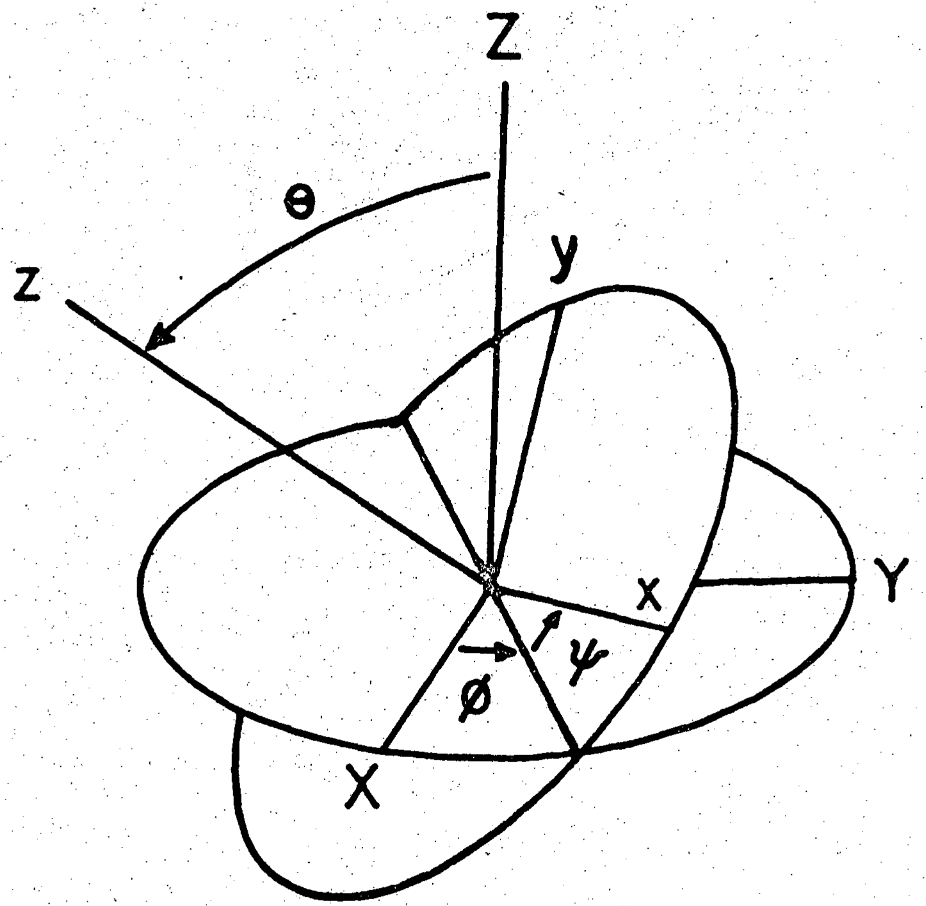


Fig. 2. Metallo - coproporphyrin isomers I and III. The symbol M stands for a divalent metal cation, Me stands for a methyl group, and P stands for propionic acid methyl ester ($(CH_2)_2$ $COOCH_3$). Both Me and P groups connect to the porphyrin ring through saturated bonds, and thus are assumed to have very little effect on the extended π orbitals which account for the visible and near-ultraviolet absorption bands.



XBL 709-5428

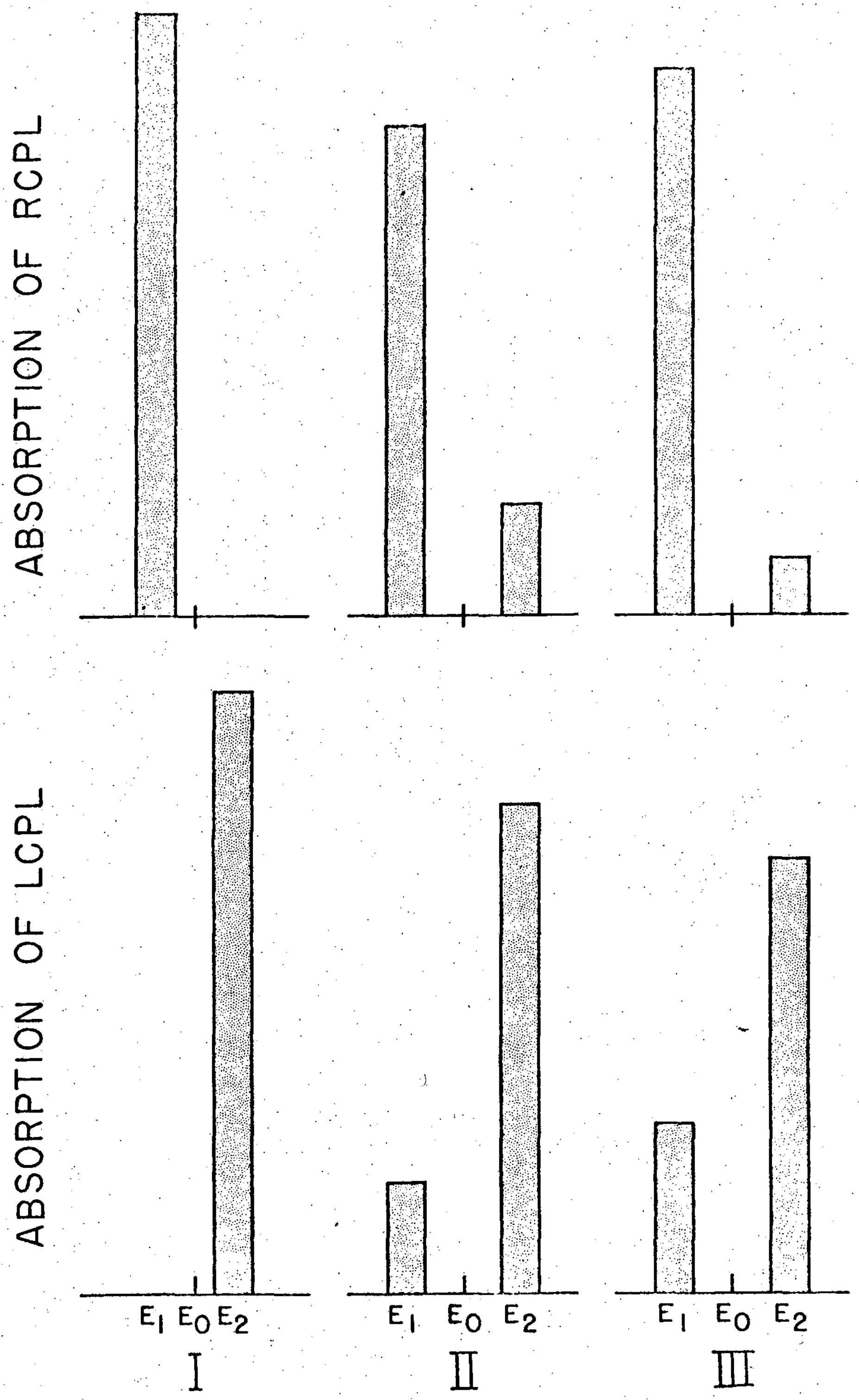
Fig. 3. The energies of states |1> and |2> as a function of $\beta H_z M_z/\Delta E_N$. When H_z goes to zero, E_1 and E_2 go to E_x and E_y.



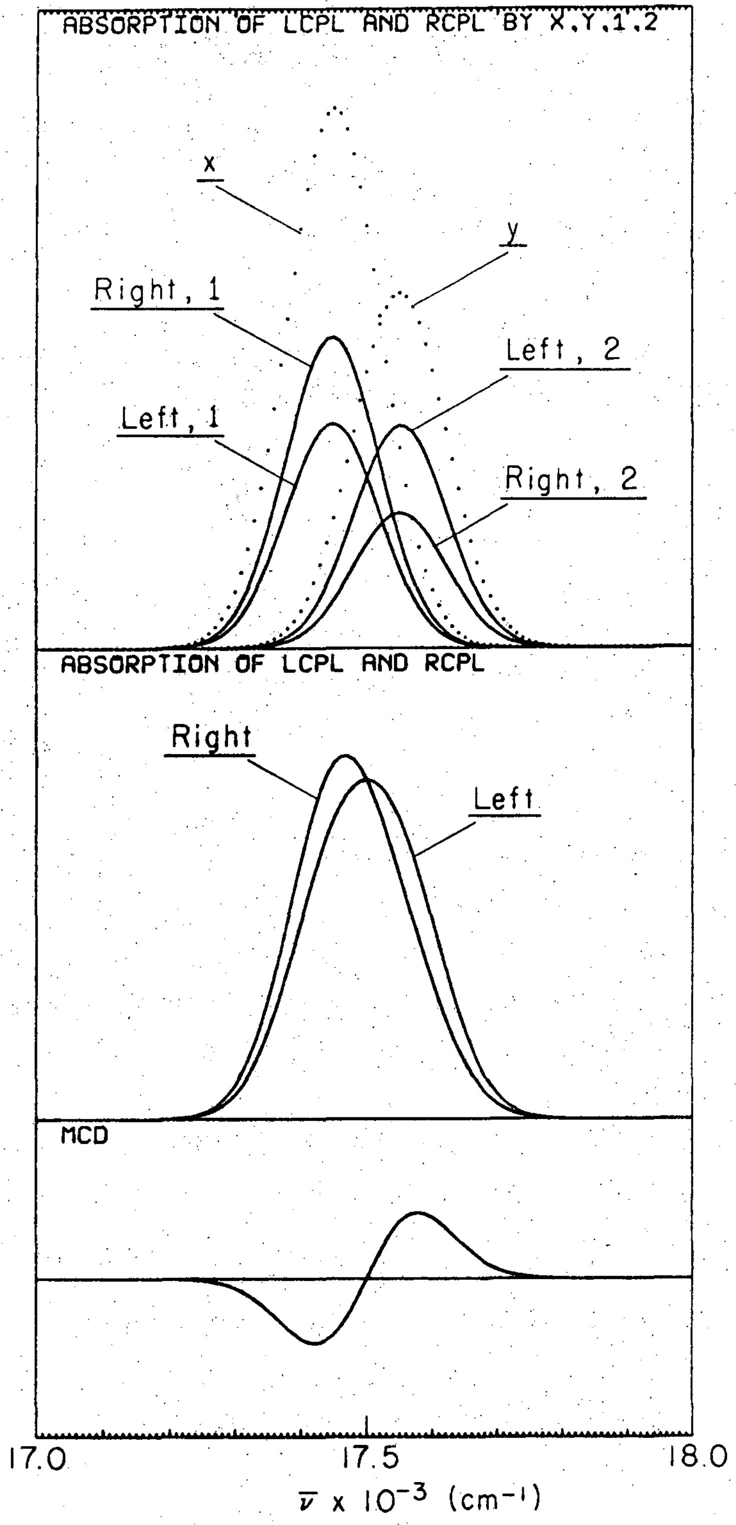
XBL709-5442

Fig. 4. The set of Euler's angles which specify the orientation of the molecule's coordinate system, xyz, with respect to the laboratory coordinate system, XYZ.

Fig. 5. Schematic representation of the absorption intensities of RCPL and LCPL of a single molecule. I. The unperturbed states are exactly degenerate ($\Delta E_N = 0$, $\Delta R^2 = 0$). In this case $\Delta E_T = \beta H_z M_z$. II. The unperturbed states are nondegenerate, but have the same intensities ($\Delta E_N \neq 0$, $\Delta R^2 = 0$). Alternatively, condition II occurs if the unperturbed states are accidentally degenerate in energy but have different intensities ($\Delta E_N = 0$, $\Delta R^2 \neq 0$). III. The unperturbed states differ in both energy and intensity ($\Delta E_N \neq 0$, $\Delta R^2 \neq 0$). The absorption intensity distribution in LCPL is asymmetric with respect to that in RCPL. However, the total absorption is the same measured in either polarization.

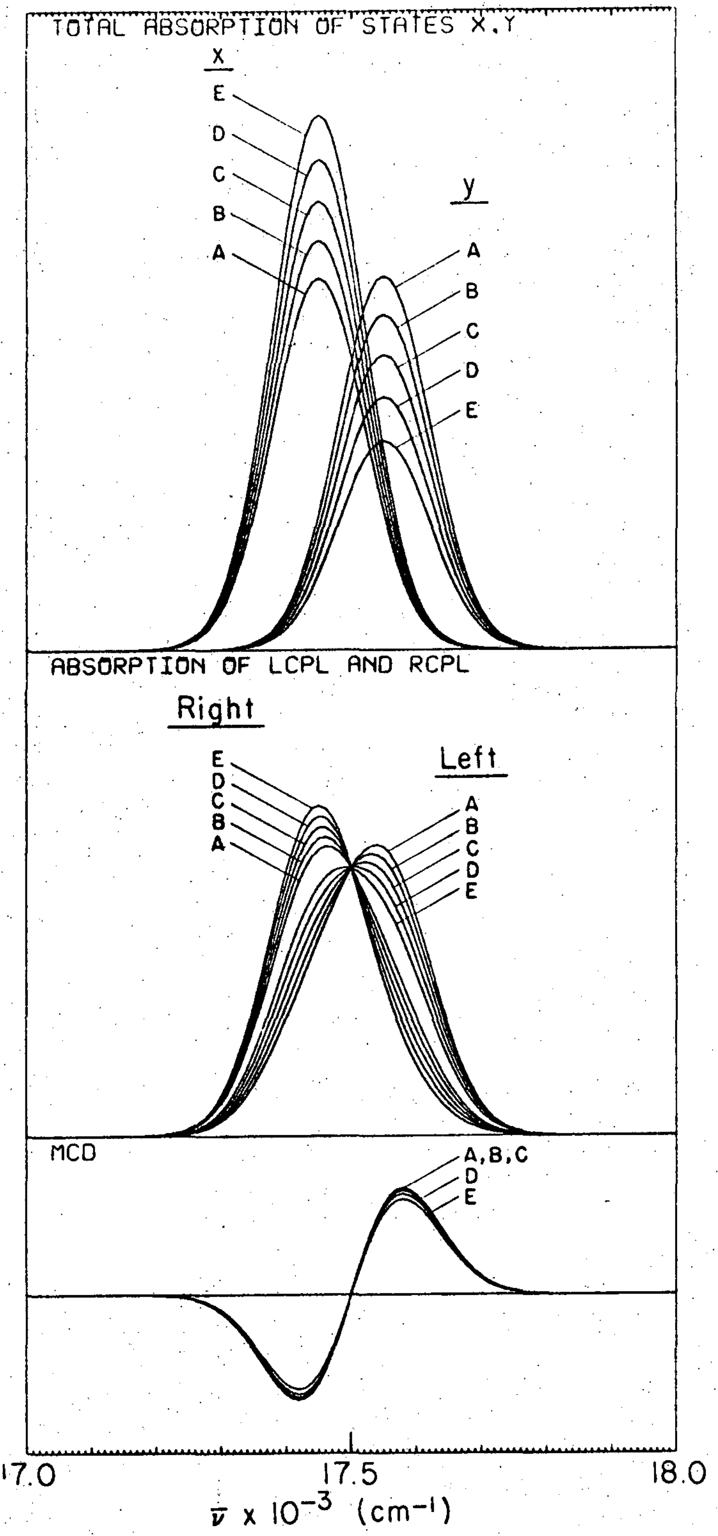


XBL 709-5448



XBL 709-5452

Fig. 6. The computed polarized absorption spectra and MCD and also the non-observable components of the unperturbed states (x and y) and the components of the RCPL and LCPL absorption spectra of the perturbed states (1 and 2). The natural splitting ($2\Delta E_N$) and the width parameter are both 100 cm^{-1}. The ratio of the y to the x band intensities is 0.653. The magnetic field is 10 Wb/m^2, and M_z is 4.5.



XBL 709-5443

Fig. 7. Decreasing the ratio R_y^2/R_x^2 while holding $R_x^2 + R_y^2$ constant changes the shapes of the RCPL and LCPL absorption bands, but has very little effect on the MCD. The values of R_y^2/R_x^2 are: A) 1, B) 0.814, C) 0.653, D) 0.512, and E) 0.389. The values of the other parameters used in the calculation are: $\Delta E_N/hc = 100$ cm^{-1}, $\Delta = 100$ cm^{-1}, $M_z = 9$, $H = 10$ Wb/m^2.

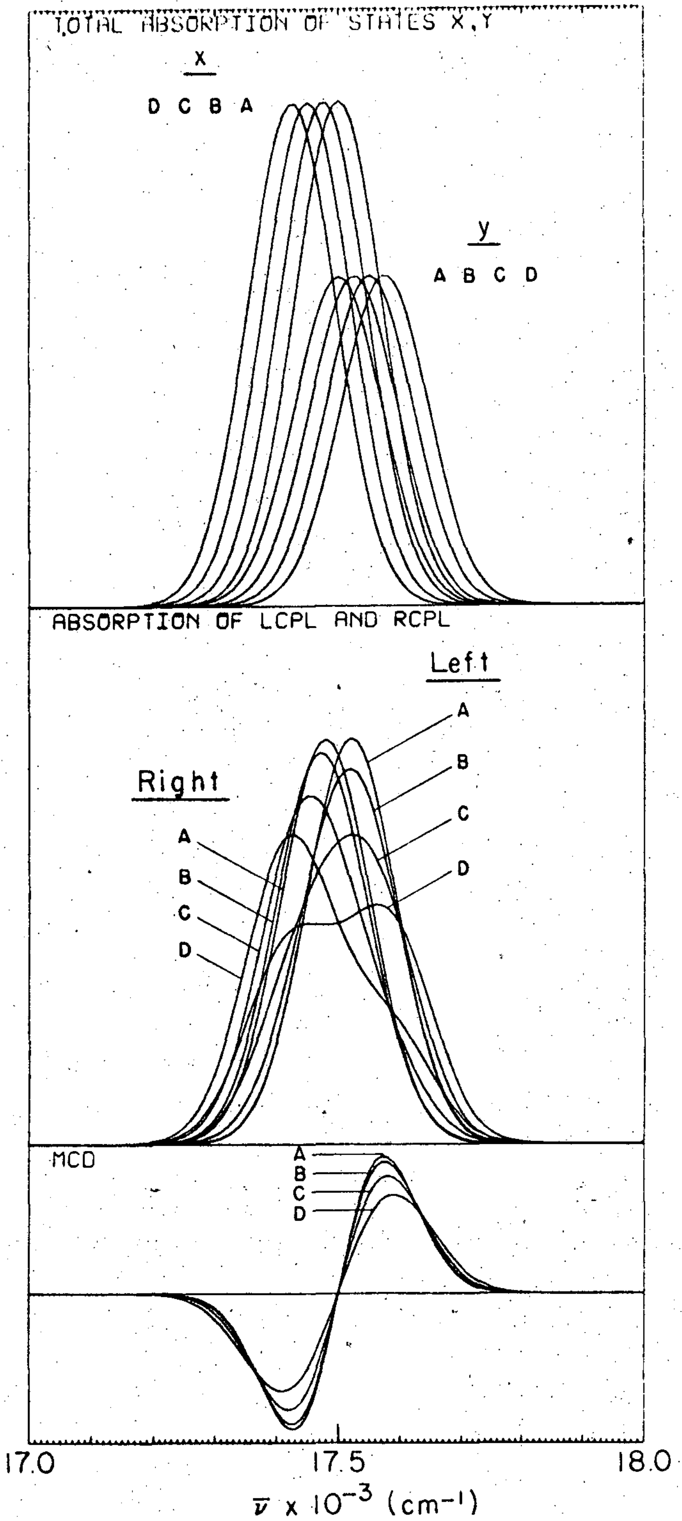
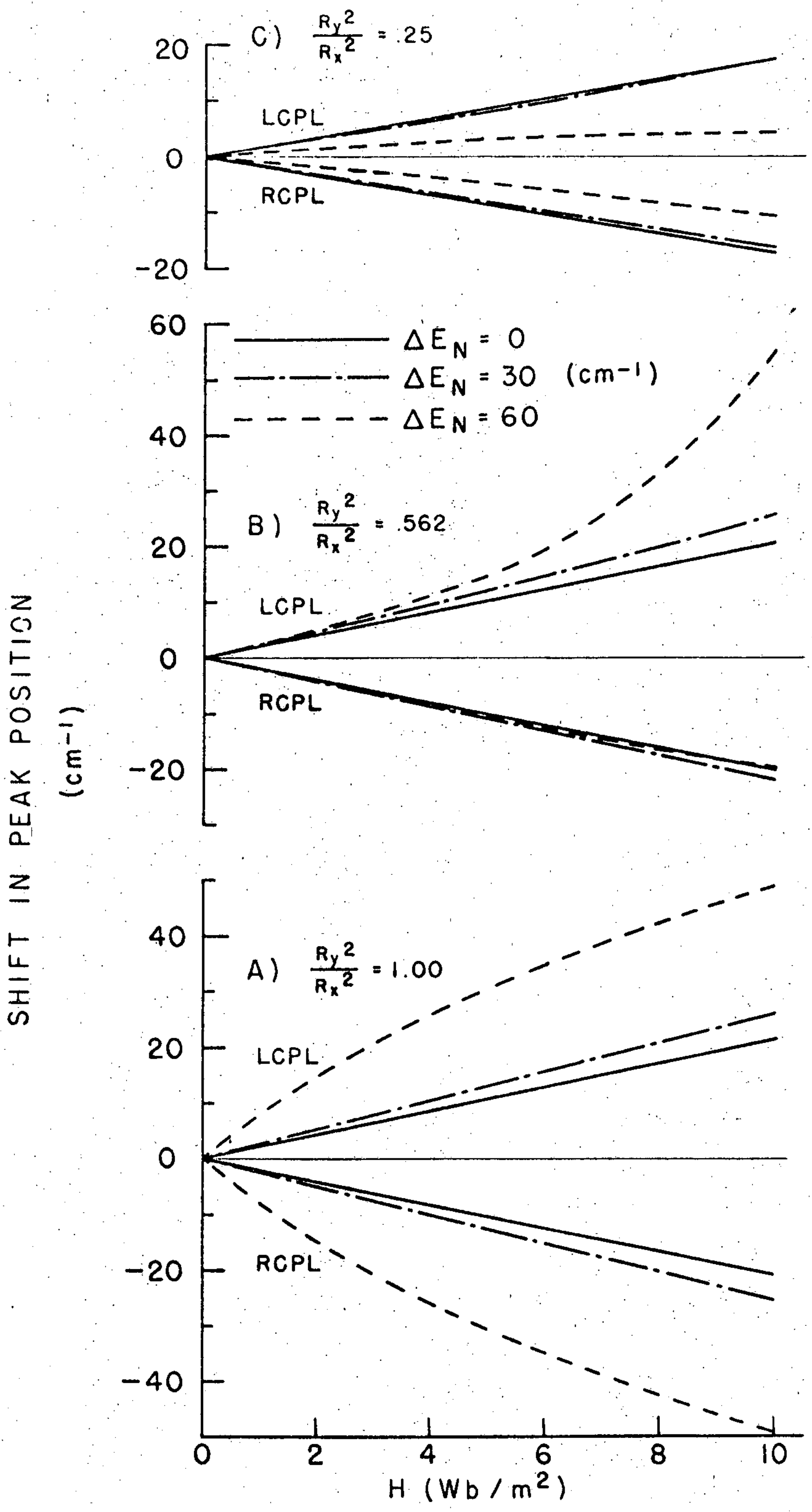


Fig. 8. The zero-field splitting increases from A to D, changing both the polarized absorption bands and the MCD. The zero-field or "natural" splittings are: A) 0, B) 50, C) 100, and D) 150 cm^{-1}. Shoulders appear in curve D for both LCPL and RCPL, and there are three isosbestic points in the MCD. Other parameters used in these calculations were: $R_y^2/R_x^2 = 0.653$, $\Delta = 100$ cm^{-1}, $M_z = 9$, and $H = 10$ Wb/m^2.



XBL 709-5450

Fig. 9. Position of the absorption peaks of the RCPL and LCPL bands calculated for ΔE_N = 0, 30, and 60 cm^{-1} and three values of R_y^2/R_x^2: A) 1.0, B) 0.562, and C) 0.25. In this computation, M_z = 9 and Δ = 100 cm^{-1}.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720