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Magnetic Circular Dichroism of Porphyrins and Derivatives. A TD-DFT Study

by

Alejandro González Peralta

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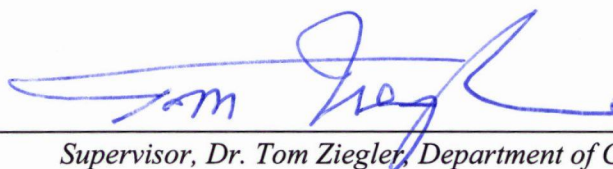
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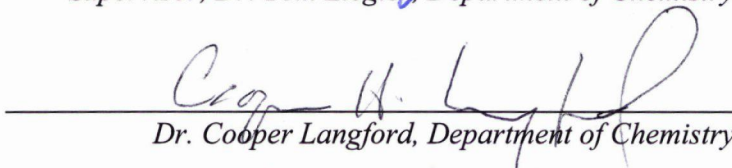
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Magnetic Circular Dichroism of Porphyrins and Derivatives. A TD-DFT Study" submitted by Alejandro González Peralta in partial fulfilment of the requirements of the degree of MASTER IN SCIENCE.



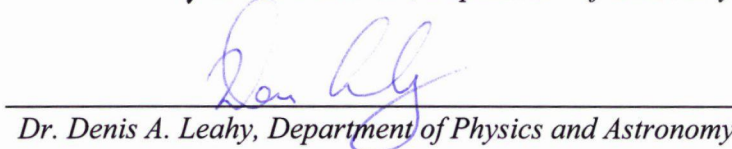
Supervisor, Dr. Tom Ziegler, Department of Chemistry



Dr. Cooper Langford, Department of Chemistry



Dr. A. Scott Hinman, Department of Chemistry



Dr. Denis A. Leahy, Department of Physics and Astronomy

*DOCTORAL STUDENTS ONLY External Examiner (or
External Reader), [FULL NAME AND INSTITUTION]*

JAN 02 - 2007

Date

Abstract

Interpretation of the Magnetic Circular Dichroism (MCD) spectra of porphyrins and derivatives has been of interest for the last decades. In this work we introduce for the first time a set of equations to allow for the characterization of the MCD spectra of porphyrins and several derivatives formed from substitutions on the m and β position. Mg, Ni, and Zn are used as metal centers of these complexes. The importance of A and B terms and how they affect the Q and B band regions of the MCD spectra of these complexes is also addressed. The simulated spectra are compared with available experimental results. TD-DFT theory was used to perform the calculations.

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Dedication

To my grandma, mom, family, and friends for all these years.

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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
TD-DFT	Time-Dependent Density Functional Theory
MCD	Magnetic Circular Dichroism
MOA	Magnetic Optical Activity
UV-Vis	Ultraviolet-Visible
STO	Slater Type Orbital
MOR	Magnetic Optical Rotation
BO	Born-Oppenheimer
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
P	Porphyrin
TPP	Tetraphenylporphyrin
OEP	Octaethylporphyrin
TAP	Tetraazaporphyrin
Pc	Phthalocyanine
M	Metal
L	Ligand
Bz	Benzene
eV	Electron Volt
E	Excitation energy

1. INTRODUCTION

A recent implementation into the Amsterdam Density Functional program [1-3] based on time-dependent density functional theory (TD-DFT) makes it possible to simulate Magnetic Circular Dichroism (MCD) spectra [4]. We present here the results from TD-DFT calculations on porphyrin related complexes. Until now many studies have been carried out at semiempirical, DFT, and *ab-initio* levels on the electronic spectra of porphyrin complexes [5-12] including one *ab-initio* study of the MCD spectra of these molecules [13]. The MCD spectra of porphyrins have also been analyzed by empirical methods [14-15].

MCD measures the difference in absorption of left and right circular-polarized light of a molecule under the influence of an external magnetic field in the direction of the propagating light. MCD is the most important of the Magneto Optical Activity (MOA) techniques and allows for the characterization of excited and ground state, symmetries. The fact that all substances are MCD active makes it an attractive technique and it has found many applications in the description of biological systems [16-18]. When a magnetic field is applied the spectra measured for the difference in absorption of left and right circular polarized light can be described by three terms, A , B and C . The A term arises from the presence of a degenerate ground and/or excited state. The A term is temperature independent while the C term, that originates as a result of a degenerate ground state, exhibits temperature dependence. The B term occurs as a result of the mixing of zero-field eigenfunctions in the presence of a magnetic field. A -terms show a derivative shape spectrum while B and C terms have a Gaussian shape and all of them

could be either positive or negative. MCD theory is well established and further details can be found in references [19-23].

Porphyrin complexes play an important roll in biological processes as diverse as respiration and photosynthesis [16]. Very often they have been used as models for chlorophylls and heme proteins [16, 24-34]. In addition they have long been used as dyes and pigments and their optical properties have pointed to potential technological applications such as linear and nonlinear optics [35-44], photodynamic therapy [45-46], electrooptics [40-44, 47-48], photonics [40-44], and catalysis [47]. The proper description of the electronic structure of porphyrins and their derivatives is also of importance for their use in optical devices.

In spite of all the experimental and theoretical studies, some aspects of the MCD spectra of porphyrins and derivatives are still not well understood. In the classification of the absorption bands observed in porphyrins and derivatives it is the convention to name the lowest energy band as the *Q* band and the following one as the *B* band or Soret band [49-55]. These two bands will be the subject of the present MCD study.

We shall begin this account by briefly discussing the basic concepts of MCD in Chapter 2 followed by an introduction to the essential features of the molecular orbital level diagrams for a number of porphyrins and their derivatives as revealed by DFT calculations and other theoretical methods in Chapter 3. After that we review (also in Chapter 3) the recorded absorption UV spectra in terms of the available orbital diagrams for some groups of porphyrines. In the last part of Chapter 3 I present the simulated MCD spectra and compare them to experimental results for porphyrins and the derivatives octaethylporphyrin and tetraphenylporphyrin. Based on these comparisons we

finally comment on previously published assignments of the Q and B bands. In Chapter 4 we provide similar discussions for tetraazaporphyrin, and phthalocyanine. Conclusions will be presented in Chapter 5.

2. METHODS AND COMPUTATIONAL DETAILS

2.1 Computational Details

All calculations were based on the Amsterdam program package ADF and its implementation of the time-dependent density functional theory [56-59]. The molecular structures were optimized based on the BP86 functional due to Becke [60] and Perdew [61]. The simulation of all UV and MCD spectra were based on TD-DFT calculations in which use was made of the SAOP potential (Statistical Averaging of different Orbital-dependent model Potentials) [62, 63]. The SAOP potential has previously been used in the simulation of UV absorption spectra of metal tetrapyrroles [64].

All the symmetry and spin allowed transitions from the A_{1g} ground state to the A_{2u} and E_u excited states were calculated in the range of 2-6 eV. For the optimization of the ground state of these complexes the core was frozen. Use was made of a triple- ζ STO valence basis set for all elements. The core shells $1s^2$ of C, N, $1s^2 2s^2 2p^6$ of Mg and $1s^2 2s^2 2p^6 3s^2 3p^6$ of Ni and Zn were frozen. A set of single- ζ STO polarization functions were used as follows: $2p$, $3d$ for H; $3d$, $4f$ for C, N; $3p$, $3d$ and $4f$ for Mg; $4s$, $4p$ and $4f$ for Ni; $4p$ and $4f$ for Zn. The symmetry was assumed to be D_{4h} for the studied molecules except for the octaethylporphyrin where a D_{2d} symmetry was used. Figure 2.1 displays the different molecules studied.

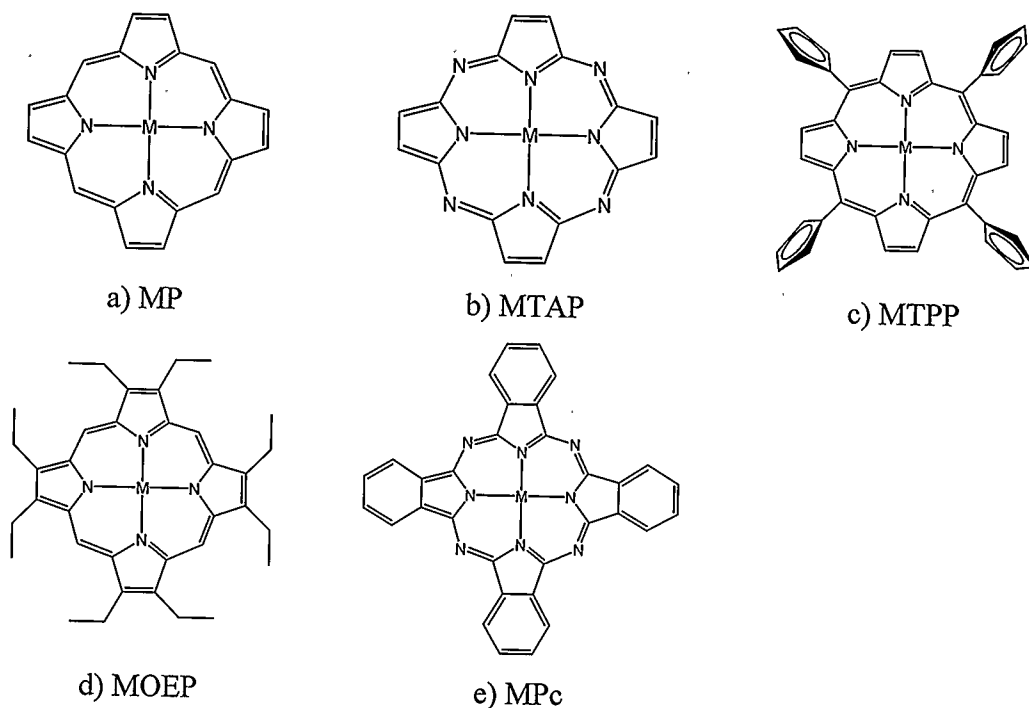


Figure 2.1. Studied ligands: a) porphyrin, b) tetraazaporphyrin, c) tetraphenylporphyrin, d) octaethylporphyrin, e) phthalocyanine. Complexes of these ligands with $M=\text{Zn}$, Mg and Ni have been studied by TD-DFT.

2.2 Introduction to General MCD Theory

Near the middle of the XIX century Michael Faraday observed that in the presence of a magnetic field an optically inactive substance will turn active by rotating plane polarized light. The phenomenon was acknowledged as Magnetic Optical Rotation (MOR). As well, when a magnetic field is applied parallel to the incident (circular polarized light) ellipticity is induced giving rise to Magnetic Circular Dichroism. The ellipticity is induced when after applying a magnetic field, the absorption coefficients of left (-) and right (+) circular polarized light change and become different.

$$\Delta k \equiv k_- - k_+ \neq 0$$

2.1

Where Δk represents the difference in absorption between left and right polarized light. Thus:

$$\Delta k(\omega, B) = \frac{4\pi\alpha^2}{hcn} \sum_r \left(\sum_a N_a \left(\left| \langle a | \mu_- | r \lambda \rangle \right|^2 - \left| \langle a | \mu_+ | r \lambda \rangle \right|^2 \right) \right) \rho_{ra\lambda}(\omega, B) \quad 2.2$$

Here α is a proportionality constant that relates the macroscopic electric field with the corresponding microscopic field (of the incident light), $\rho_{ra\lambda}(\omega, B)$ is the density of states function for the transition of a to r at frequency ω . Further h is the Planck constant, c is the speed of light, and n is the refractive index. Also ω is the frequency at which the absorption is measured. N_a is the number of molecules absorbing in the ground state.

The expression in Equation 2.2 gives Δk as a function of ω for a transition from the ground state which in the absence of a magnetic field is n_0 times degenerate with the wave functions $(a_1^o, a_2^o, \dots, a_{n_0}^o)$ to the excited state λ , which without a magnetic field is n_λ degenerate with the wave functions $(\lambda_1^o, \lambda_2^o, \dots, \lambda_{n_\lambda}^o)$. In the presence of the magnetic field the ground state functions are $(a_1, a_2, \dots, a_{n_0})$ and they might not be degenerate. Likewise, after the inclusion of the magnetic field the excited state wave functions are given by $(\lambda_1, \lambda_2, \dots, \lambda_{n_\lambda})$ and they might not be degenerate either.

Finally the one electron operators μ_- and μ_+ expressed in terms of the electron coordinates (x, y, z) are given by $\mu_- = 1/\sqrt{2}(x + iy)$ and $\mu_+ = 1/\sqrt{2}(x - iy)$. If the electric

dipole is expressed in the more common Cartesian coordinates using the relation given above and a non-degenerate ground state is considered then the equation would be expressed as:

$$\Delta k(\omega, B) = \frac{8\pi\alpha^2}{hcn} \mathfrak{S}_m \sum_r N_a \langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \rho_{ra\lambda}(\omega, B) \quad 2.3$$

Since we are assuming that $\Delta k(\omega, B)$ is proportional to the magnetic field then we need to find the first derivative of Equation 2.3 with respect to the magnetic field. Since the terms before the summation signs are constants or magnetic-field independent then only three terms could possibly depend on the magnetic field. Those are N_a , $\langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle$ and $\rho_{ra\lambda}(\omega, B)$ such as:

$$\begin{aligned} \frac{\delta \Delta k(\omega, B)}{\delta B} &= \frac{8\pi\alpha^2}{hcn} \mathfrak{S}_m \sum_r \left(N_a \langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \frac{\rho_{ra\lambda}(\omega, B)}{\delta B} + \right. \\ &N_a \frac{\delta (\langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle)}{\delta B} \rho_{ra\lambda}(\omega, B) + \\ &\left. \frac{\delta N_a}{\delta B} \langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \rho_{ra\lambda}(\omega, B) \right) \end{aligned} \quad 2.4$$

These three terms are associated with the experimental A , B and C terms. Furthermore, an expression could be found for the derivative of the density of states with the magnetic field expanding the density of states in a power series of B_z which affords

$$\rho_{a\lambda}(\omega, B_z) = \rho_{a\lambda}(\omega, 0) + \left(\frac{\delta \rho_{a\lambda}(\omega, B_z)}{\delta \omega} \right) \left(\frac{\delta \omega_{r\lambda}}{\delta B_z} \right) \cdot B_z + \dots \quad 2.5$$

And keeping the terms only to first order,

$$\rho_{a\lambda}(\omega, B_z) \approx \rho_{a\lambda}(\omega, 0) + \left(\frac{\delta \rho_{a\lambda}(\omega, B_z)}{\delta \omega} \right) \left(\frac{\delta \omega_{r\lambda}}{\delta B_z} \right) \cdot B_z \quad 2.6$$

From Equation 2.6 an expression for the derivative of the density of states with respect to the magnetic field can be obtained if making use of the rigid-shift approximation.

$$\frac{\delta \rho_{a\lambda}(\omega, B_z)}{\delta B_z} = \frac{\delta \omega_{r\lambda}}{\delta B_z} \left(-\frac{\delta \rho_{a\lambda}(\omega, 0)}{\delta \omega} \right) \quad 2.7$$

Substituting Equation 2.7 into 2.4 affords

$$\begin{aligned} \frac{\delta \Delta k(\omega, B_z)}{\delta B_z} &= \frac{8\pi\alpha^2}{hcn} \mathfrak{G}_m \sum_r \left(N_a \frac{\delta \omega_{r\lambda}}{\delta B_z} \langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \left(-\frac{\delta \rho_{a\lambda}(\omega, 0)}{\delta \omega} \right) + \right. \\ &\quad \left(N_a \frac{\delta \left(\langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \right)}{\delta B_z} + \right. \\ &\quad \left. \left. \frac{\delta N_a}{\delta B_z} \langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \right) \rho_{a\lambda}(\omega) \right) \end{aligned} \quad 2.8$$

This in turn can be written as

$$\frac{\delta \Delta k_{a\lambda}(\omega, B_z)}{\delta B_z} = \frac{8\pi\alpha^2}{hcn} N_a \left(-\mathcal{A}_{a\lambda} \frac{\delta \rho_{0\lambda}(\omega)}{\delta \omega} + \left(\mathcal{B}_{a\lambda} + \frac{C_{a\lambda}}{kT} \right) \rho_{0\lambda}(\omega) \right) \quad 2.9$$

If we define $\mathcal{A}$, $\mathcal{B}$ and $\mathcal{C}$ as

$$\mathcal{A} = 2\mathfrak{O}_m \sum_r \left(\frac{\delta \omega_{r\lambda}}{\delta B_z} \langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \right) \quad 2.10$$

$$\mathcal{B} = 2\mathfrak{O}_m \sum_r \left(\frac{\delta \left(\langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \right)}{\delta B_z} \right) \quad 2.11$$

$$\mathcal{C} = 2\mathfrak{O}_m \sum_r \left(\frac{\delta N_a}{\delta B_z} \langle 0 | \mu_x | r\lambda \rangle \langle r\lambda | \mu_y | 0 \rangle \right) \quad 2.12$$

After finding the orientationally averaged expressions and using the Born-Oppenheimer (BO) approximation we obtain Equations 2.13 – 2.16.

$$\mathcal{A} = iC \sum_{\substack{\alpha\alpha' \\ \lambda\lambda'}} \left(\langle J_\lambda | (L+2S) | J_{\lambda'} \rangle \delta_{\alpha\alpha'} - \langle A_{\alpha'} | (L+2S) | A_\alpha \rangle \delta_{\lambda\lambda'} \right) \cdot \left(\langle A_\alpha | \mu | J_\lambda \rangle \times \langle J_{\lambda'} | \mu | A_{\alpha'} \rangle \right) \quad 2.13$$

$$\begin{aligned} \mathcal{B} = 2\mathfrak{O}_m C \sum_{\alpha\lambda} \left[\sum_{\substack{K_\kappa \\ (K \neq A)}} \frac{\langle K_\kappa | (L+2S) | A_\alpha \rangle}{W_K - W_A} \cdot \left(\langle A_\alpha | \mu | J_\lambda \rangle \times \langle J_\lambda | \mu | K_\kappa \rangle \right) \right. \\ \left. + \sum_{\substack{K_\kappa \\ (K \neq J)}} \frac{\langle J_\lambda | (L+2S) | K_\kappa \rangle}{W_K - W_J} \cdot \left(\langle A_\alpha | \mu | J_\lambda \rangle \times \langle K_\kappa | \mu | A_\alpha \rangle \right) \right] \quad 2.14 \end{aligned}$$

$$\mathcal{C} = -iC \sum_{\alpha\alpha'\lambda} \langle A_{\alpha'} | (L+2S) | A_\alpha \rangle \cdot \left(\langle A_\alpha | \mu | J_\lambda \rangle \times \langle J_\lambda | \mu | A_{\alpha'} \rangle \right) \quad 2.15$$

$$\mathcal{D} = C \sum_{\alpha\lambda} \left| \langle A_\alpha | \mu | J_\lambda \rangle \right|^2 \quad 2.16$$

Equations 2.13 – 2.16 represent the $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ and $\mathcal{D}$ (dipole strength) parameters. A more profound analysis of the parameters of importance for the systems studied will be given in the sections that follow.

In the equations above we are considering an excitation from the ground state which in the absence of B has the degenerate many electrons wave function A_α ($\alpha=1\dots n_a$) to the excited state with the degenerate wave functions J_λ without a magnetic field. All other excited states are represented by the field free wave functions K_κ .

For an in-depth derivation of each of these equations and an extensive explanation of the MCD formalism, applications, examples, etc., consult Reference [19].

2.3 Basic TD-DFT

In order to solve the time-dependent problem formally defined by the Kohn-Sham equations and make use of the time-dependent first-order density change due to an external potential we can express the TD-DFT working equation as follow:

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} C & 0 \\ 0 & -C \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad 2.17$$

In the previous equations ω and $-\omega$ are eigenvalues of the former equation while X and Y are the eigenvectors which must satisfy:

$$\begin{pmatrix} X^\dagger & Y^\dagger \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = 1 \quad 2.18$$

The matrices A and B are further expressed in terms of the Fock and the density matrix elements as:

$$A_{ai,bj} = \frac{\varepsilon_a - \varepsilon_i}{n_b - n_j} \delta_{ij} \delta_{ab} - K_{ai,bj} \quad 2.19$$

$$B_{ai,bj} = -K_{ai,bj} \quad 2.20$$

$$K_{ai,bj} = \int dr \int dr' \phi_a^*(r) \phi_i(r) \left(\frac{1}{r-r'} + f_{xc}(r, r', \omega) \right) \phi_b(r') \phi_j^*(r') \quad 2.21$$

$$C_{ai,bj} = \frac{1}{n_b - n_j} \delta_{ij} \delta_{ab} \quad 2.22$$

Where f_{xc} is the exchange correlation kernel and can be expressed as the $t \rightarrow \omega$

$$\text{Fourier transform of } f_{xc}(r, r', t - t') = \frac{\delta V_{xc}(r, t)}{\delta \rho_\tau(r', t')}.$$

As a convention, the sub indices i and j are used for occupied orbitals while a and b are used for virtual orbitals. p and q are general orbital indices. The eigenvalues from Equation 2.17 provide the excitation energies and the transition densities which are identified with $(X + y) \propto S^{-1/2} F_\lambda$ and can be defined as the coupling of the electronic ground state with a given excited state.

2.4 The Calculation of MCD Parameters by TD-DFT

In order to determine X and Y we need to solve the eigenvalue problem shown in Equation 2.23 [56, 65, 66].

$$\Omega F = \omega^2 F \quad 2.23$$

where the excitation energies ω are associated with the square root of the eigenvalues and Ω and using the definitions from above,

$$\Omega = -S^{-1/2} (A+B) S^{-1/2} \quad 2.24$$

$$\begin{aligned} S &= -C(A-B)^{-1} C \\ &= \frac{\delta_{ab} \delta_{ij}}{\epsilon_b - \epsilon_j} \end{aligned} \quad 2.25$$

And the normalized eigenvectors are then related to X and Y as follows

$$(X+Y) = \frac{1}{\sqrt{\omega}} S^{-1/2} F \quad 2.26$$

$$(X-Y) = \sqrt{\omega} S^{1/2} F \quad 2.27$$

When solving Equations 2.13 – 2.16, most of the terms can be obtained from the solution of Equation 2.23, [56, 65, 66]. As stated before the eigenvalues of Equation 2.23 allow the determination of $\mathcal{W}_k$. In the calculation of $\langle A|\mu|K \rangle$ Equation 2.28 is used.

$$\langle A|\mu|K\rangle = \sum_{ai} \sqrt{\frac{\varepsilon_i - \varepsilon_a}{W_K}} \mu_{ai} F_{ai}^K \quad 2.28$$

where ε_a and ε_i are the molecular orbital energies of a and i respectively and μ_{ai} are the matrix elements of the electric dipole moment operator with orbitals i and a , while F_{ai}^K is an element of the K^{th} F -vector related to the one-electron excitation from orbital a to orbital i .

Another parameter found in Equations 2.13 – 2.16 is the matrix elements of the angular momentum operator $\langle A|L|K\rangle$ with the form

$$\langle A|L|K\rangle = \sum_{ai} \sqrt{\frac{W_K}{\varepsilon_i - \varepsilon_a}} L_{ai} F_{ai}^K \quad 2.29$$

The other terms are electric dipole and angular momentum matrix elements involving only excited states of the type $\langle J|\mu|K\rangle$ and $\langle J|L|K\rangle$ respectively. If $J = K$ then Equation 2.30 is used (see Reference 67).

$$\begin{aligned} \langle J|\mathcal{O}|J\rangle - \langle A|\mathcal{O}|A\rangle = & \frac{1}{2} \left[\sum_{aij} \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a) + W_J^2}{W_J \sqrt{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)}} F_{ai}^J F_{aj}^J \mathcal{O}_{ij} - \right. \\ & \left. \sum_{abi} \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b) + W_J^2}{W_J \sqrt{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)}} F_{ai}^J F_{bi}^J \mathcal{O}_{ab} \right] \quad 2.30 \end{aligned}$$

In a similar manner, the off-diagonal elements between excited states can be obtained through Equation 2.31, which is a generalization of Equation 2.30.

$$\begin{aligned}
\langle J | \mathcal{O} | K \rangle = & \frac{1}{2} \left[\sum_{aij} \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a) + W_J W_K}{\sqrt{W_J W_K (\varepsilon_i - \varepsilon_a)(\varepsilon_j - \varepsilon_a)}} F_{ai}^J F_{aj}^J \mathcal{O}_{ij} - \right. \\
& \left. \sum_{abi} \frac{(\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b) + W_J W_K}{\sqrt{W_J W_K (\varepsilon_i - \varepsilon_a)(\varepsilon_i - \varepsilon_b)}} F_{ai}^J F_{bi}^J \mathcal{O}_{ab} \right]
\end{aligned}
\tag{2.31}$$

Using the equations revised in this section allow then for the calculation of Equations 2.13 – 2.16.

2.5 Illustrative Examples

In order to exemplify some of the terms described by Equations 2.13 – 2.16 we introduce a few simple examples.

2.5.1 Origin of A-terms

In the first case we have a non-degenerate ground state described in spectroscopic notation as 1S and a singlet excitation occurs to the degenerate excited state 1P , Figure 2.2, when no magnetic field is applied. At this point, only the A-term will be considered. As stated before, $\Delta k(\omega)$ is the result of the difference in absorption between the left and the right polarized light and will result in no signal as shown in Figure 2.2a. This is so since absorption of right and left polarized light will exactly cancel. A magnetic field B is then applied allowing for an immediate shift in energy of the excited states and change in absorption frequencies of left and right circular polarized light. Under this condition, a

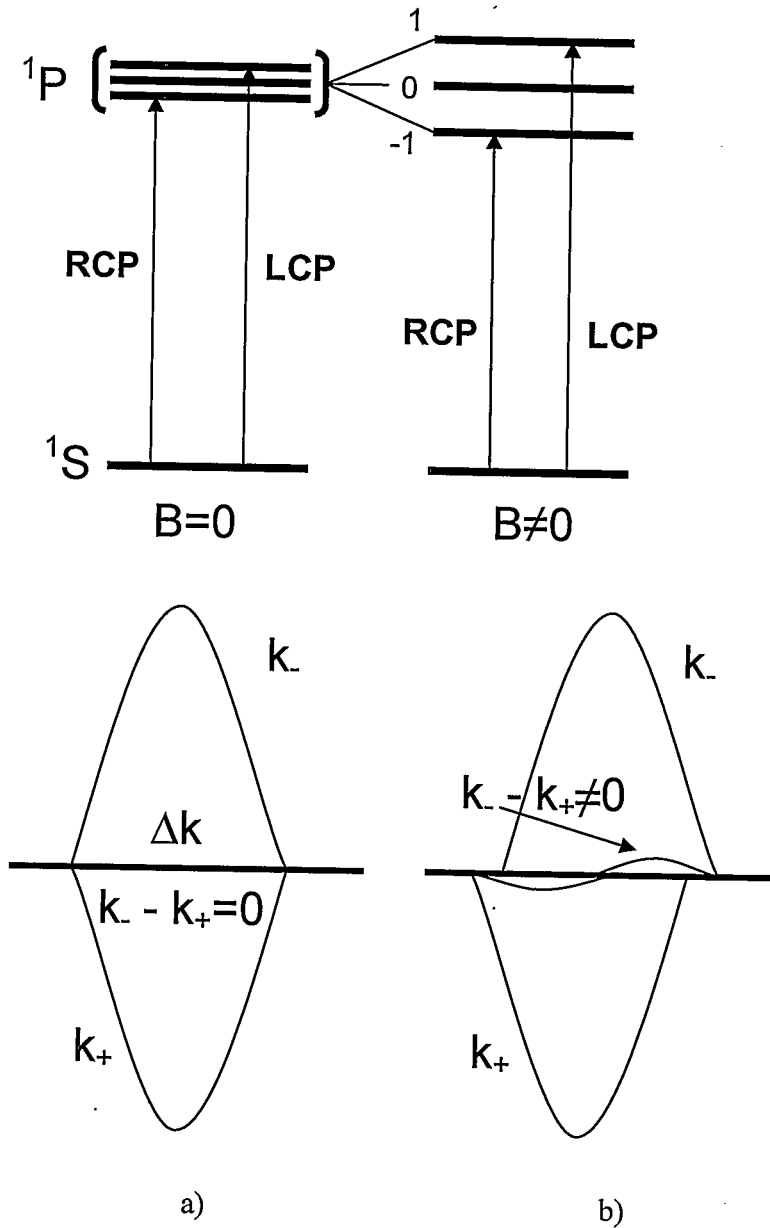


Figure. 2.2. a) The absorption of RCP and LCP light for $^1P \rightarrow ^1S$ with $B=0$. The difference $\Delta k=0$ as the degenerate 1P levels are equally occupied. b) The absorption of RCP and LCP for $^1P \rightarrow ^1S$ with $B \neq 0$. The difference $\Delta k \neq 0$ as the 1P levels are split by magnetic field and thus occupied differently.

derivative shaped signal will be recorded similar to that shown in Figure 2.2b. Applying Equation 2.13 to this particular situation would yield:

$$\mathcal{A} = iC \left(\left\langle {}^1P_{-1} \left| \tilde{L} \right| {}^1P_1 \right\rangle \right) \cdot \left(\left\langle {}^1S \left| \tilde{\mu} \right| {}^1P_{-1} \right\rangle \times \left\langle {}^1P_1 \left| \tilde{\mu} \right| {}^1S \right\rangle \right) \quad 2.32$$

Furthermore, we can find an expression for the commonly used A/D term if applying this situation to Equation 2.16 for the dipole strength leaving

$$\frac{\mathcal{A}}{\mathcal{D}} = -i \left\langle {}^1P_{-1} \left| \tilde{L} \right| {}^1P_1 \right\rangle \quad 2.33$$

2.5.2 Origin of the C term

Another interesting situation could be present when we have a degenerate ground state and an excitation occur to a non-degenerate excited state as shown in Figure 2.3. Under these conditions only the C term will be considered and using Equation 2.15 we obtain

$$C = -iC \left\langle {}^1P_{-1} \left| L \right| {}^1P_1 \right\rangle \cdot \left(\left\langle {}^1P_1 \left| \mu \right| {}^1S \right\rangle \times \left\langle {}^1S \left| \mu \right| {}^1P_{-1} \right\rangle \right) \quad 2.34$$

It is straightforward to find an expression for the C/D term. In Figure 2.3 the magnetic field will split 1P into ${}^1P_{+1}$, 1P_0 and ${}^1P_{-1}$ with ${}^1P_{-1}$ of lowest energy. At a finite temperature ${}^1P_{-1}$ will be more populated than ${}^1P_{+1}$. As a consequence k_{-1} will be larger than k_{+1} . Thus, $\Delta k \equiv k_{-} - k_{+}$ will be negative. With increasing temperature Δk will diminish as the two levels become equally populated. The shape of the observed C -term

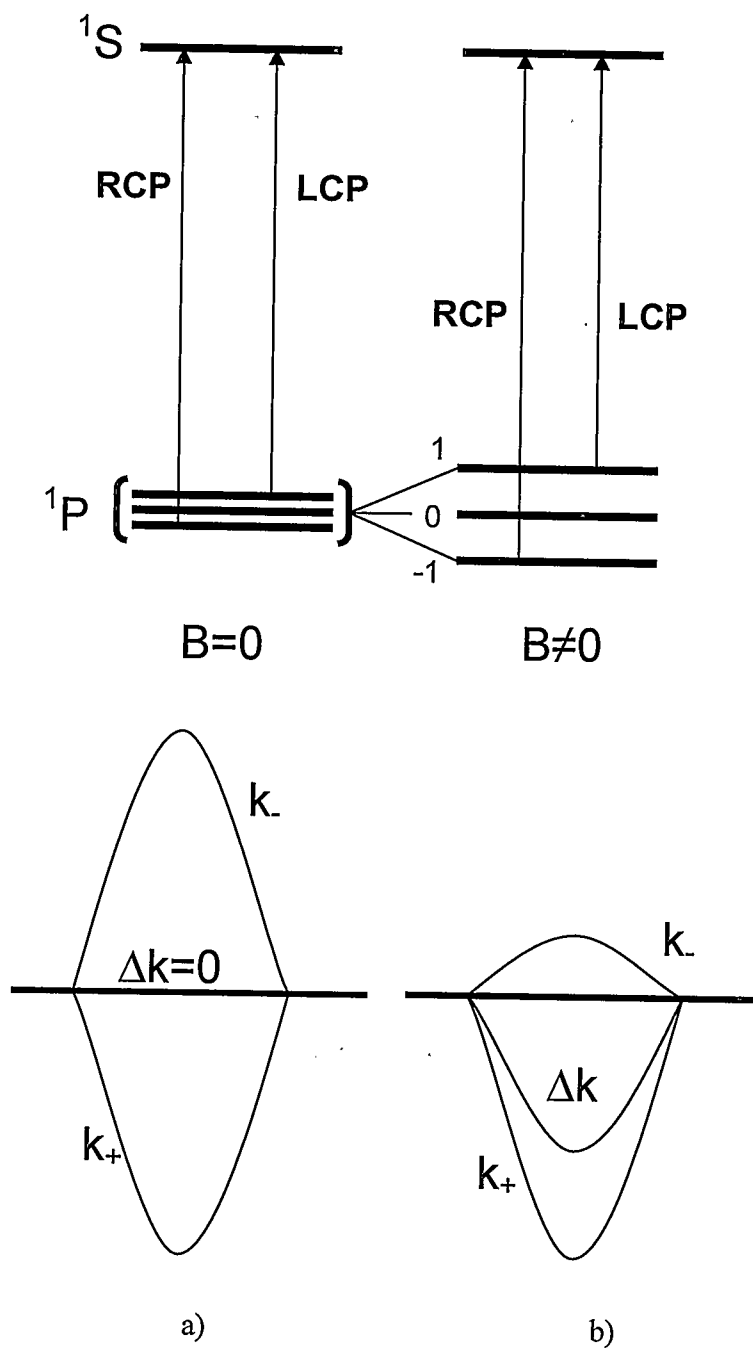


Figure 2.3. a) Absorption of RCP and LCP light at $B=0$. The difference Δk is zero b) The absorption of RCP and LCP for $B \neq 0$. The difference $\Delta k \neq 0$ due to the energy splitting of 1P .

will depend on whether spin-orbital coupling is considered or not. Here it is shown with a Gaussian shape although it can also be observed with an asymmetric derivate shape.

2.5.3 B-term for degenerate level split by perturbations

Let us now consider a system where, after applying a small perturbation, for instance an electric field in the x-direction or a geometrical distortion, degeneracy is lost at the excited state, Figure 2.4. Under these conditions, with the magnetic field in the z-direction, the only term contributing to the MCD spectra would be the B term due to mixing of states by the magnetic field. Consider Figure 2.4, where in case *a* an unperturbed system is observed ($E_x = 0, B = 0$), in case *b* $E_x \neq 0$ and $B = 0$ whereas in case *c* ($E_x \neq 0, B \neq 0$). It is of interest to consider only how the interaction of the two non-degenerate excited states due to the magnetic field will contribute to the MCD spectra. For cases *a* and *b*, $\Delta k = 0$. However for case *c* $\Delta k \neq 0$. The magnetic field, in case *c*, allows the mixing of the components of the excited state (nE_{ix}, nE_{iy}) and using Equation 2.14 leads to

$$\mathcal{B}(nE_{ix}, nE_{iy}) = \left(2\mathcal{G}_m C \frac{\langle nE_{ix} | L | nE_{iy} \rangle}{W_{nE_{iy}} - W_{nE_{ix}}} \cdot \left(\langle A_{2,u} | \mu | nE_{ix} \rangle \times \langle nE_{iy} | \mu | A_{2,u} \rangle \right) \right) \cdot (\rho(nE_{ix}) - \rho(nE_{iy})) \quad 2.35$$

Equation 2.35 is obtained for a system with D_{4h} symmetry where excitations from the ground state A_{1g} to the excited state nE_u take place. The small perturbation splits the degeneracy of the x and y components of the excited state into nE_{ux} and nE_{uy} which

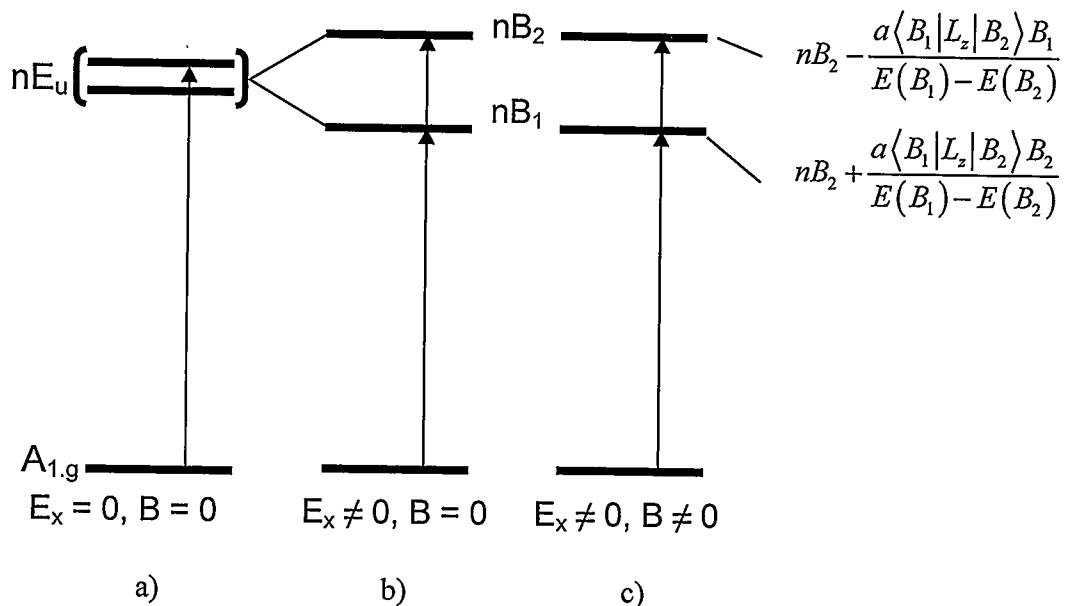


Figure 2.4. Splitting of the components of the excited state after applying a small perturbation.

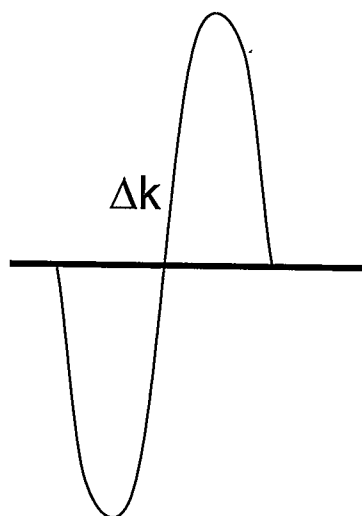


Figure 2.5. Observed pseudo-A term due to the mixing of components of the

same excited state.

further mixing gives rise to B -shaped bands in the correspondent MCD spectrum. These two do not cancel each other since they occur at different absorption energies resulting in the observation of a pseudo- A term. Therefore $\Delta k \neq 0$, see Figure 2.5. A similar band would be observed for $E_x = 0$, $B \neq 0$. However, it would now be attributed to the A term.

2.5.4 B -term between two close excited states

Besides interactions among components of the same excited state split by a perturbation, the mixing of components from different excited states nE_u and pE_u where $p \neq n$, can make B terms observable in MCD spectra. Here we are still assuming a D_{4h} symmetry for our sample system. In this case we will assume that the mixing between the x and y components of the same excited state is part of the A term, Figure 2.6. Equation 2.36 is then obtained after applying the assumed conditions to Equation 2.14.

$$\mathcal{B}(nE_{ux}, pE_{uy}) = 4\mathcal{S}_m C \sum_{p=1, p \neq n} \frac{\langle nE_{ux} | L | pE_{uy} \rangle}{W_{pE_{uy}} - W_{nE_{ux}}} \cdot (\langle A_{2,u} | \mu | nE_{ux} \rangle \times \langle pE_{uy} | \mu | A_{2,u} \rangle) \quad 2.36$$

Equation 2.36 accounts for the mixing of the n^{th} excited state with a number of p excited states due to the magnetic field. The farther apart the interacting states are, the smaller the contribution to the MCD spectra and the smaller the observed B term (Gaussian-shaped, Figure 2.7).

Having introduced the basics of MCD and TD-DFT we now proceed to present and discuss our results for the calculations on porphyrins and derivatives.

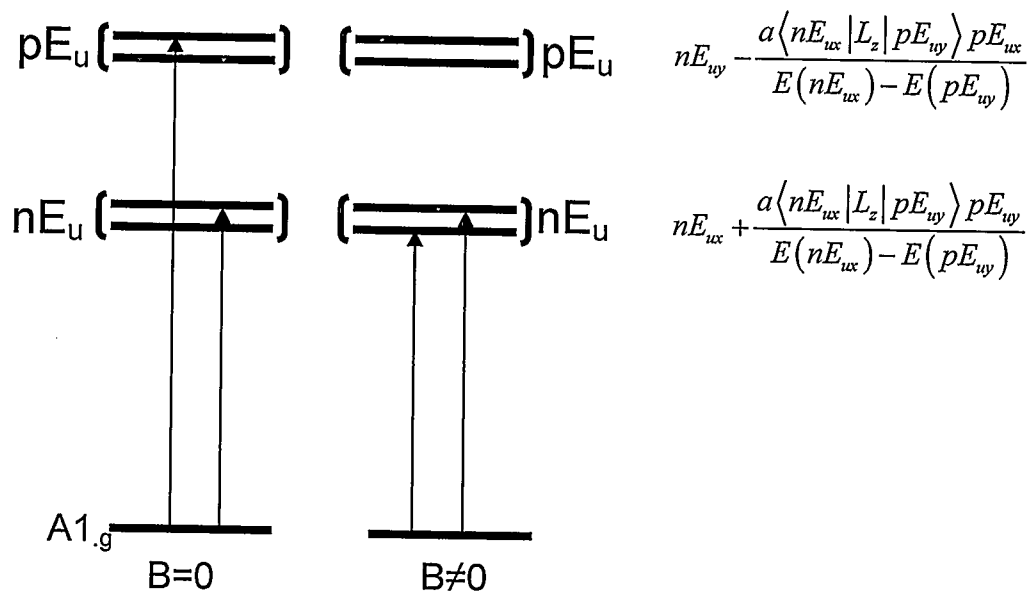


Figure 2.6. Origin of the B terms due to the mixing of components of excited states n and p .

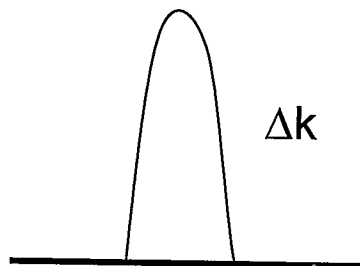


Figure 2.7. Observed Gaussian-shaped band due to the B -terms from the mixing of excited states n and p .

3. RESULTS AND DISCUSSION FOR METAL PORPHYRINS

We shall begin our discussion of the MCD spectra of porphyrins and their derivatives by briefly reviewing the orbital levels and absorption spectra of these systems. The systems discussed here and in the preceding chapters are shown in Figure 2.1.

3.1 General Discussion of the Molecular Orbitals of Porphyrins and their Derivatives

Two of the three complexes (MP and MTPP) studied in this chapter were considered to have a D_{4h} symmetry in line with previous experimental and theoretical works. The other one was considered to have D_{2d} symmetry. All complexes were placed in the XY plane with the C_4 axis pointing in the z -direction. Figures 3.1-3.5 display the calculated MO energy level diagrams for MP, MTPP, and MOEP discussed in this chapter as well as MTAP and MPc discussed in Chapter 4.

We found for all the systems the lowest unoccupied ligand-based level to be represented by a π^* orbital of e_{1g} symmetry, Figure 3.6. The HOMO, on the other hand, was found to be, in general, an a_{1u} orbital for MTAP and MPc, and an a_{2u} orbital for porphyrins and substituted porphyrins (*i.e.* MP, MTPP and MOEP), Figure 3.6. In the later case the a_{2u} and a_{1u} orbitals lie so close in energy that they can be considered as degenerate.

It follows from the energy level diagrams in Figures 3.1-3.5 that the higher occupied and lower unoccupied orbitals for complexes of a given ligand are similar in terms of energy and symmetry. It is thus clear that the metal center only has a minor influence on these orbitals. In line with this observation we also find the two highest occupied orbitals of H_2L with $b_{1,u}$ and a_u symmetry in the D_{2h} point group to be very similar in composition and energy to the highest occupied orbital of ML with $a_{2,u}$ and $a_{1,u}$ symmetry in the D_{4h} point group. Also as $a_{2,u}$ drops considerably in energy below $a_{1,u}$ for ML in going from L=P to L=TAP or Pc, the $b_{1,u}$ orbital drops below $a_{1,u}$ in the corresponding series of HL_2 systems. We also note that the nearly degenerate LUMO's of H_2L with $b_{3,g}$, $b_{2,g}$ symmetries correspond closely to the degenerate set of LUMO's in ML with e_g symmetry.

In spite of these observations complexes containing a Ni center have an energy level diagram that differs somewhat from the rest of the studied systems for the same ligand. This difference is a consequence of the empty valence d -orbital located below the lowest empty ligand orbital and four occupied d -orbitals situated among the highest occupied π^* ligand levels, see Figure 3.1 for NiP. The empty d -based orbital of $b_{1,g}$ symmetry has a 57% contribution from $d_{x^2-y^2}$ while the highest occupied d -level of $a_{1,g}$ symmetry has a contribution of 89% d_{z^2} . The next two d -levels transforming as $e_{1,g}$ have a contribution of 57% from the d_{yz} and d_{xz} each while the lowest d -level belonging to the $b_{2,g}$ representation have a 92% contribution from the d_{xy} . Of all the mentioned d orbitals the $d_{x^2-y^2}$ is of special importance since it is involved actively in transitions located in the B band. We indicate the d -levels in Figures 3.1-3.5 in terms of $d_{x^2-y^2}$, d_{z^2} , etc. rather than their symmetry labels, $b_{1,g}$, $a_{1,g}$, etc. Furthermore, the d -levels were not added to the

numbering of the levels ($1e_g$, $2e_g$, etc.) in order to facilitate the comparison between ML systems with different metals ($M=\text{Zn}$, Mg , Ni). In the section that follows we shall refer to the lowest unoccupied ligand orbital ($2e_g$) as the LUMO although the empty $d_{x^2-y^2}$ level is of lower energy for $M=\text{Ni}$.

A closer look at the diagrams for different ligands reveals that the N substitution in the inner ring at the m position lowers the energy of the HOMO and LUMO. However, the energy difference between these orbitals remains the same. Figure 3.7 displays the position of the m sites. An important consequence of the N substitution in the m position (MTAP or MPc) or the phenyl addition in the β position, (MPc), is that the accidental degeneracy of the $a_{1,u}$ and $a_{2,u}$ levels is lifted. This effect is stronger for the N-substitution than for the phenyl addition.

3.2 General Discussion of the UV-Vis Absorption Spectra of Metal Porphyrins and Derivatives

The absorption spectrum of metal porphyrins and their derivatives has been studied extensively by experimental methods. Theoretically it has also been explored to a certain extent. It is not our objective here to give an extensive discussion of the absorption spectra of these molecules since it already has been done [10, 12, 64, 67, 68]. Hence, before discussing their MCD spectra, we will briefly discuss the assignments provided for the Q and B bands

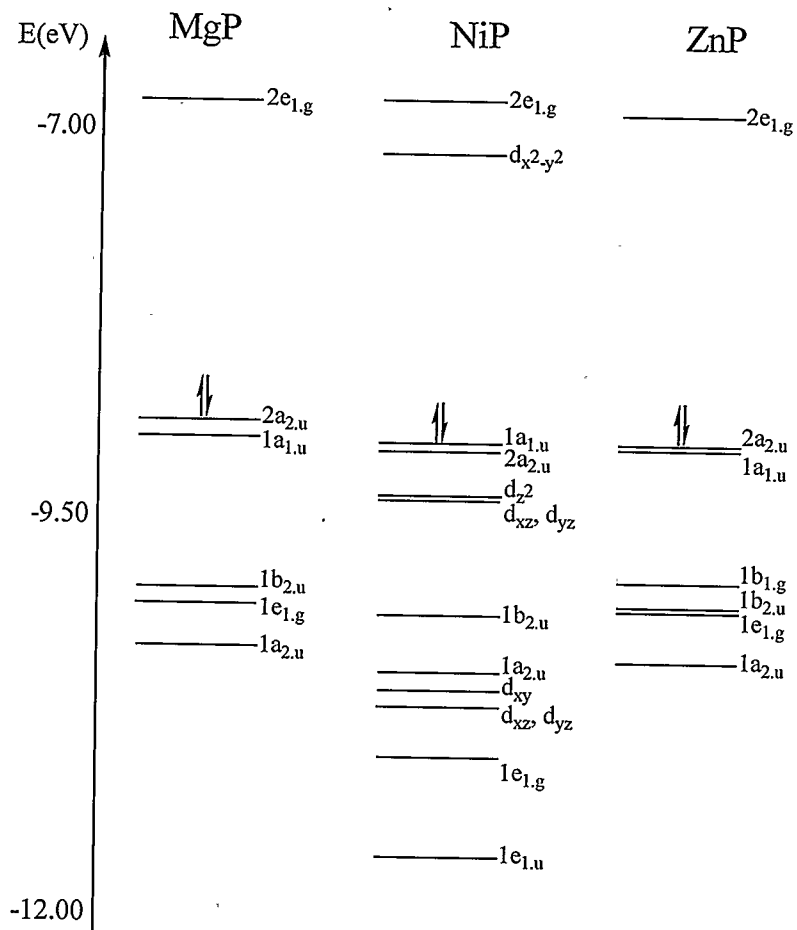


Figure 3.1. Molecular Orbital energy levels diagram corresponding to MP.

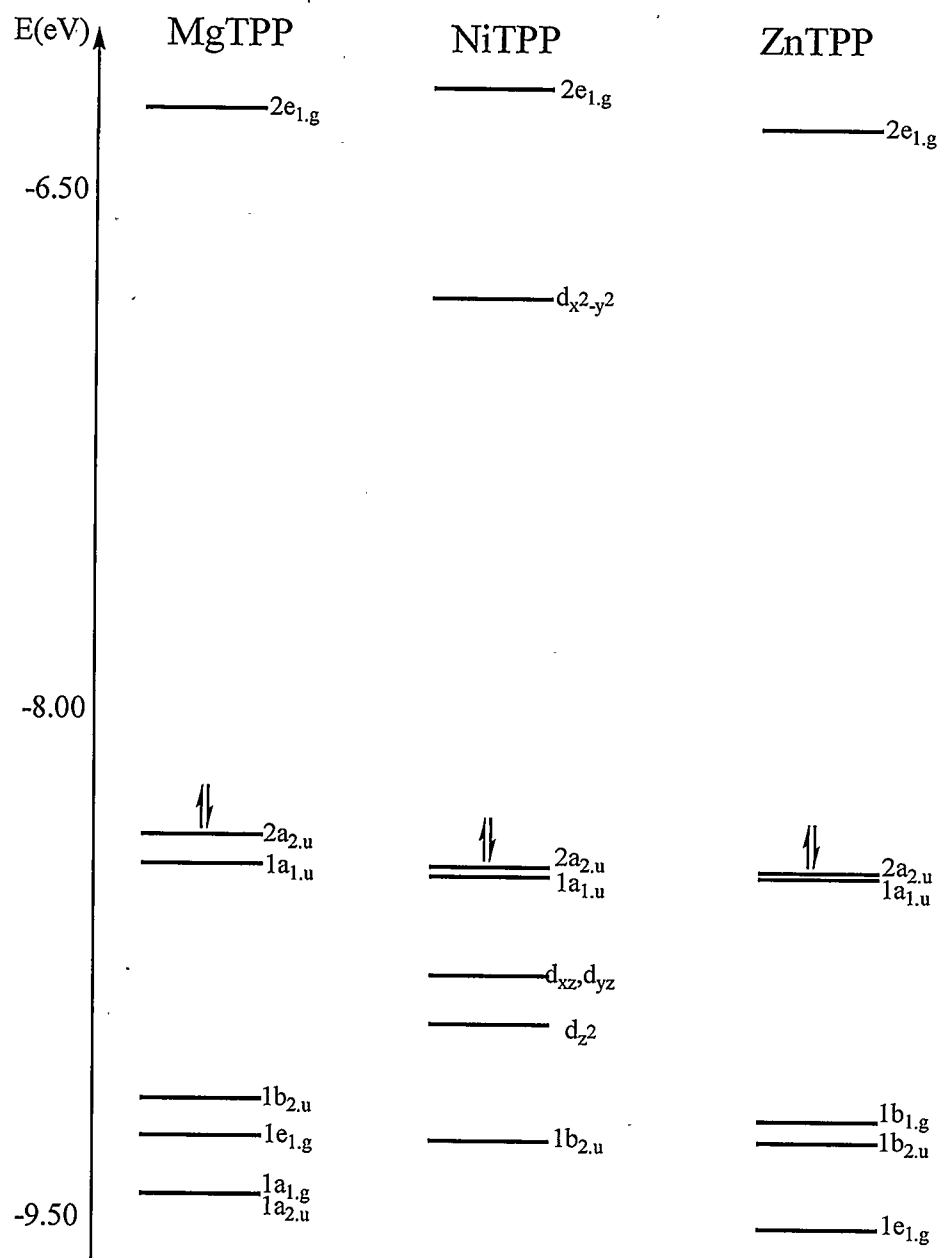


Figure 3.2. Molecular Orbital energy levels diagram corresponding to MTPP.

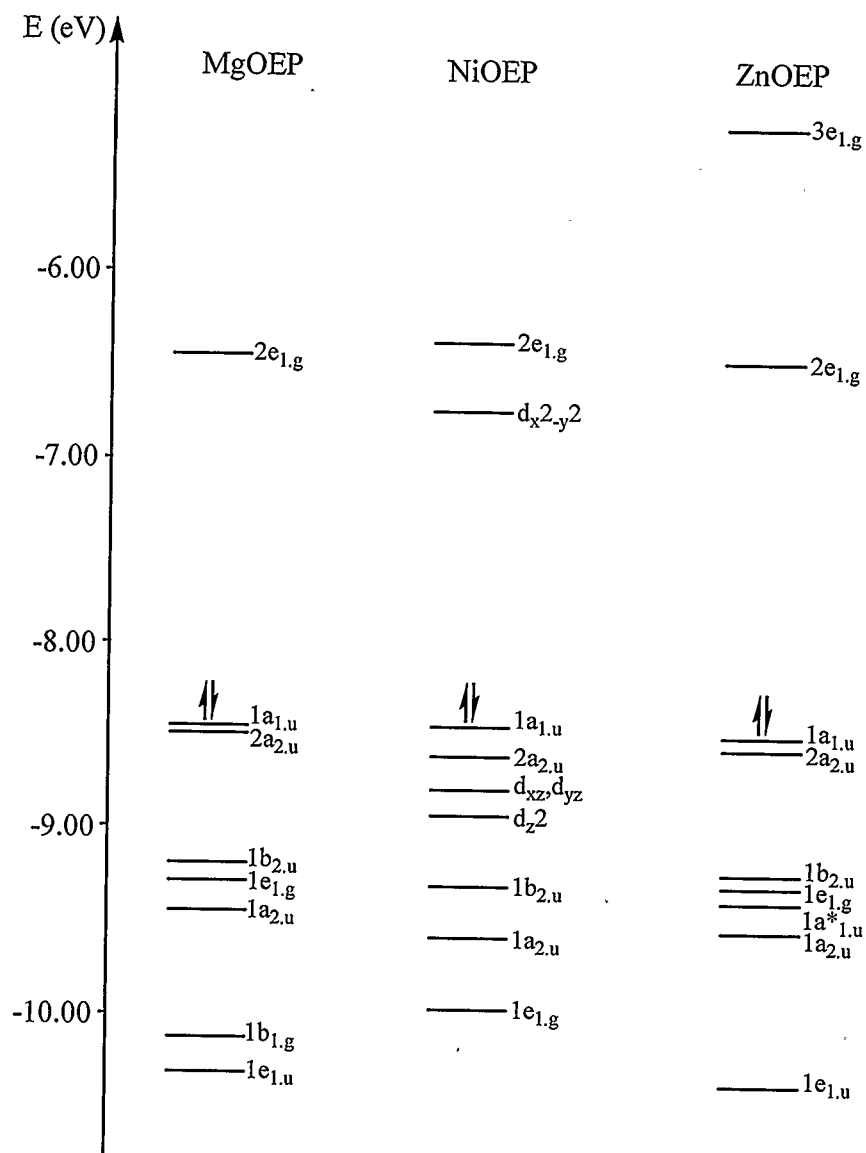


Figure 3.3. Molecular Orbital energy levels diagram corresponding to MOEP. Orbitals are expressed using D_{4h} symmetry notation instead of D_{2d} .

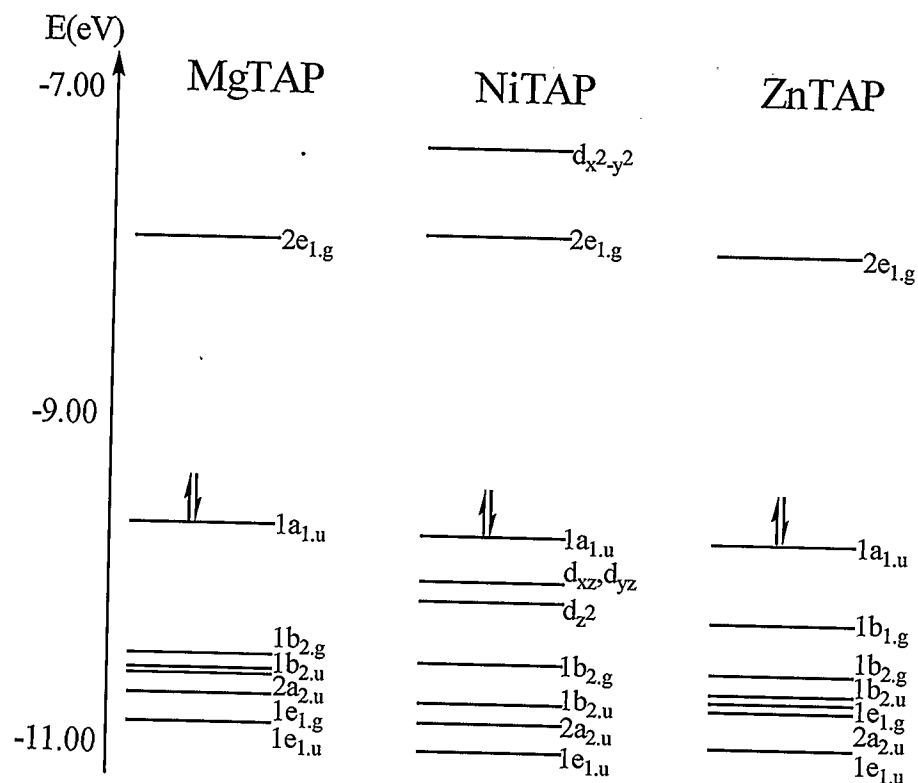


Figure. 3.4. Molecular Orbital energy levels diagram corresponding to MTAP.

The only dipole and spin allowed transitions from the ${}^1A_{1g}$ singlet ground state are to the ${}^1A_{2u}$ and 1E_u singlets, of which only the ${}^1A_{1g} \rightarrow {}^1E_u$ transitions are observed in the absorption spectra. The oscillator strength of the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transitions is very close to zero in the experimental range so the absorption spectra will be dominated by transitions of the former type. These transitions take place from/to orbitals in the x - y plane to/from orbitals pointing in the z -direction, depending on the ligand and the metal center. The z -polarized transitions ${}^1A_{1g} \rightarrow {}^1A_{2u}$ are said to be responsible for the broadening of the B band [4, 69].

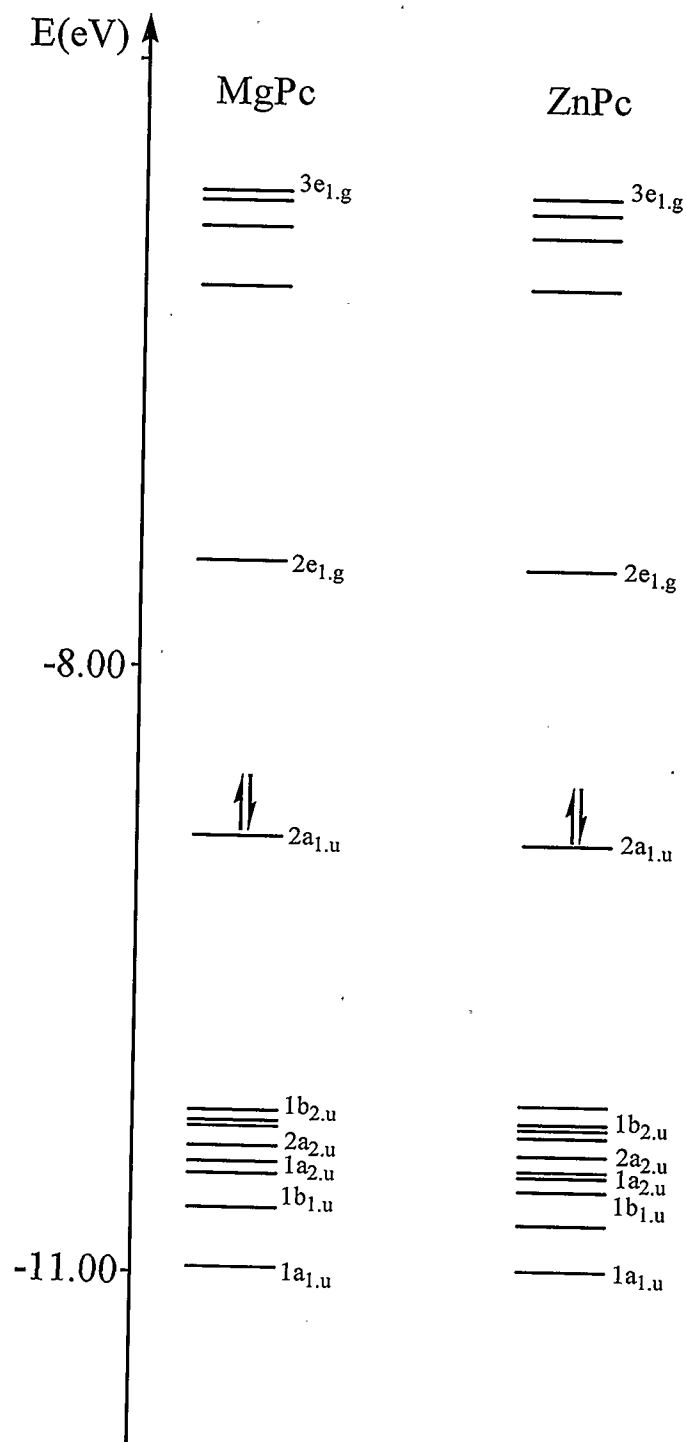


Figure 3.5 Molecular Orbital energy levels diagram corresponding to MPc. Only the more relevant orbitals have been noted.

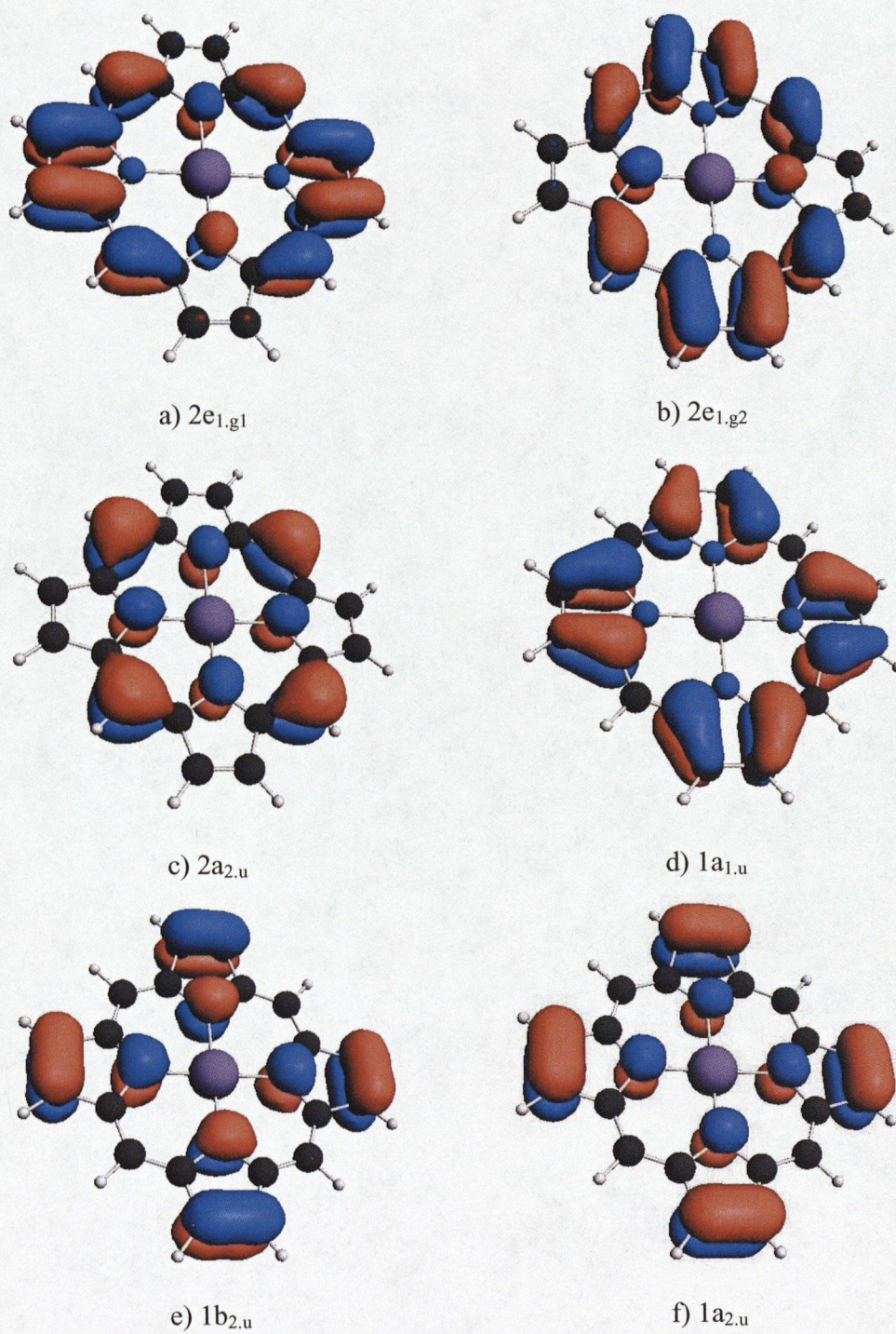


Figure 3.6. Most relevant ligand orbitals for porphyrin systems.

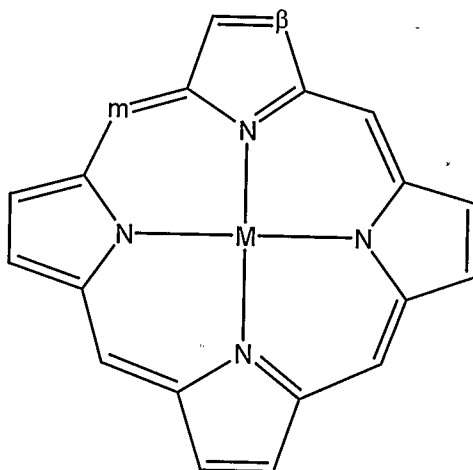


Figure 3.7. Porphyrin molecule where the β and m positions are indicated.

The first peak in the absorption spectra of a metal porphyrin and its derivatives is termed the Q band. In the MP, MTPP and MOEP systems, it consists of one excitation made up of two one-electron transitions from occupied orbitals of $a_{1,u}$ and $a_{2,u}$ symmetries, respectively, to the e_g LUMO. In MP (and to a somewhat lesser degree in the MTPP and MOEP systems) the $a_{1,u}$ and $a_{2,u}$ orbitals (see Figure 3.1-3.3 and 3.6) are nearly degenerate for reasons explained by Gouterman [49-55] and $a_{1,u} \rightarrow e_g$ and $a_{2,u} \rightarrow e_g$ contribute equally to the excitation of the Q band. Furthermore, as shown by Gouterman [49-55], the two one-electron transitions have equal contributions of opposite signs to the transition dipole which makes the absorption of the Q band weak [49-55]. In the nitrogen substituted porphyrins MPc and MTAP, the $a_{1,u}$ orbital is much higher in energy than the $a_{2,u}$ (Figures 3.5, 3.6). As a consequence, the Q band is now mostly made up of the $a_{1,u} \rightarrow e_g$ transition. The Q band is more intense due to the lack of a cancellation from the $a_{2,u} \rightarrow e_g$ transition to the transition dipole moment.

Experimentally, the Soret or B band has been observed to have from one to three peaks (B_1 , B_2 and B_3). The number of resolved peaks depends on the complex studied as well as on the resolution of the spectroscopic technique applied. In our work and previous studies one-electron transitions of the type $a_{1,u} \rightarrow e_g$ and $a_{2,u} \rightarrow e_g$ always contribute with high intensity. Here e_g could be either of the first two unoccupied ligand-based levels whereas $a_{1,u}$ and $a_{2,u}$ are the occupied ligand based levels of highest energy. Additional excitations involve one-electron transitions from the highest occupied $b_{1,u}$ and $b_{2,u}$ (Figure 3.1-3.3, 3.6) ligand orbitals to the lowest unoccupied ligand based e_g and $b_{1,u}$ orbitals. Another important one-electron transition contributing to the B band is the transition from the occupied e_g ligand based level to the unoccupied ligand orbital $b_{1,u}$. It follows from the above discussion that the assignment of the B band varies from complex to complex as we shall see when we discuss the individual systems in the next sections in connection with their MCD spectra.

3.3 Mg, Ni, and Zn Porphyrins

To proceed with the main objective of our work, we shall begin by discussing our simulations of MCD spectra for complexes containing porphyrin ligands.

3.3.1 UV-Vis Absorption Spectra of Mg, Ni and Zn Porphyrins

We compare in this section available experimental UV-Vis absorption spectra for metal porphyrins (MP) with theoretical predictions. An in-depth theoretical analysis of

the corresponding MCD spectra will be introduced in the following sections. Related ligands such as tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP) [12, 15, 70] will be discussed in separate sections.

The experimental absorption spectra for the three MP systems exhibit two peaks in the Q region and a single more intense peak in the B region of their UV-Vis absorption spectra. The peaks in the Q band have been attributed, by experimentalists, to the same electronic excitation but different vibronic transitions (vibronic coupling) and are often referred to as Q_{00} and Q_{01} . We find in agreement with this interpretation only one calculated excitation in the experimentally observed range for the Q-band.

The Q band of ZnP has been observed from 2.03 eV and up to 2.23 eV and the B band is observed from 2.95 and up to 3.18 eV depending on the experimental conditions [71 - 74], Table 3.1. The Q band of MgP has been observed at 2.14 eV and 2.20 eV and the B band is located at 3.18 eV [75, 76]. NiP has a slight shift to the blue in the Q band (2.28 eV) while the B band is observed at 3.18 eV [75], see Table 3.1. For the porphyrin complexes, the NiP has the highest calculated oscillator strength with 0.006 while MgP and ZnP were calculated to be both 0.001.

Table 3.1. Calculated excitation energies (eV), oscillator strength (f), A, A/D, B and B/D terms for MP (M=Mg, Ni, Zn).

Complex Symmetry	Exc. Energ. (eV)		Composition	%	f	A (D ² μ _B)	A/D (μ _B)	B	B/D	Assign.	
	exp.	calc.									
MgP	E _u	2.14 ^a , 2.2 ^b	2.23	2a2.u → 2e1.g 1a1.u → 2e1.g	54.15 44.58	0.001	0.07	5.46	-1.25	-0.63 X 10 ⁻³	Q
	E _u	3.18 ^a	3.23	1b2.u → 2e1.g 1a1.u → 2e1.g 2a2.u → 2e1.g	75.02 14.11 6.69	0.383	-18.78	-1.80	-3.18 X 10 ³	-1.97 X 10 ³	
	E _u		3.30	1a1.u → 2e1.g 2a2.u → 2e1.g 1b2.u → 2e1.g 1a2.u → 2e1.g	28.98 28.63 22.73 16.82	0.972	11.08	0.43	4.28 X 10 ³	1.067	B
	E _u	2.28 ^a	2.37	1a1.u → 2e1.g 2a2.u → 2e1.g	50.56 48.24	0.006	1.26	5.48	0.97	0.03 X 10 ⁻³	Q
	A _{2,u}		2.98	1b2.u → dx ² -y ²	99.89	0.000	0.00	0.00	-0.35	-0.47 X 10 ⁻³	
	E _u	3.18 ^a	3.21	2a2.u → 2e1.g 1a1.u → 2e1.g 1e.u → dx ² -y ²	43.17 41.94 7.23	1.042	8.90	0.31	0.16 X 10 ³	0.03 X 10 ³	B
	E _u		3.41	1b2.u → 2e1.g 1e1.g → 1b1.u	96.02 1.40	0.000	-0.62 X 10 ⁻³	-2.75	-0.62	-17.79 X 10 ³	
	E _u	2.03 ^c , 2.21 ^d , 2.23 ^e , 2.18 ^f	2.28	2a2.u → 2e1.g 1a1.u → 2e1.g	52.10 46.63	0.001	0.33	5.49	-1.30	-0.14 X 10 ⁻³	Q
	E _u	2.95 ^c , 3.09 ^d , 3.18 ^e , 3.13 ^f	3.25	1b2.u → 2e1.g 1a1.u → 2e1.g 2a2.u → 2e1.g	68.44 17.54 10.05	0.496	-21.76	-1.62	-3.69 X 10 ³	-1.78 X 10 ³	B
E _u		3.32	1b2.u → 2e1.g	29.88	0.943	-3.67	-0.15	4.57 X 10 ³	1.18 X 10 ³		

2a2.u	->	2e1.g	29.31
1a1.u	->	2e1.g	27.13
1a2.u	->	2e1.g	10.30

^a Ref 69, ^b Ref 71, ^c Ref 70, ^d Ref 72, ^e Ref 73, ^f Ref 74.

The agreement between calculated and experimental absorption energies for MP are excellent, Table 3.1. According to our calculations only one excitation contributes to the Q band and it is made up of the two one-electron transitions $2a_{2,u} \rightarrow 2e_g$ and $1a_{1,u} \rightarrow 2e_g$. They have contributions to the intensity of opposite sign that largely cancel so that the Q band appears as weak. The more intense B band consists according to our calculations of two electronic transitions made up of one-electron excitations from $1a_{1,u}$, $2a_{2,u}$, $2b_{2,u}$ and $1a_{2,u}$ to $2e_g$.

3.3.2 Detailed Theoretical Discussion of the MCD Parameters A and A/D in Mg, Ni and Zn Porphyrins

The metal porphyrins investigated here have a non-degenerate ${}^1A_{1,g}$ ground state which precludes C terms in the MCD spectra. On the other hand, the presence of degenerate ${}^1E_{1,u}$ excited states is likely to give rise to A terms in the MCD spectra of the ${}^1A_{1,g} \rightarrow {}^1E_{1,u}$ excitations and we shall in the following give a detailed discussion of the A and A/D terms for porphyrins. B terms, that are always possible, will be discussed later. The Q band, as seen in Table 3.1, always consists of transitions from $1a_{1,u}$ and $2a_{2,u}$ orbitals to $2e_{1,g}$ orbitals while the B band also includes transitions from the $1a_{2,u}$ and the $1b_{2,u}$ to the $2e_{1,g}$. The main difference here for the various metal centers ($M = \text{Mg, Ni, Zn}$) is the relative weight by which the one-electron excitations contribute to the Q and B bands. A general expression for A/D for these systems is readily obtained from Chapter 2 and showed in Equation 3.1 where ${}^1E_{1,u}^x$ and ${}^1E_{1,u}^y$ are the excited states involved in the Q and B band excitation.

$$\frac{A}{D} = -\langle \Psi(1E_{1,u}^x) | \hat{L}_z | \Psi(1E_{1,u}^y) \rangle \quad 3.1$$

As stated before, only one-electron transitions of the kind $a_{1,u} \rightarrow e_g$ and $a_{2,u} \rightarrow e_g$ contribute to the Q band so we can express the states of Equation 3.1 in terms of the orbitals and the coefficients of the contribution of these orbitals to the given excited state. In addition to the transitions contributing to the Q band, the transition $b_{2,u} \rightarrow e_g$ contributes to the B band. In order to obtain a generalized equation for the Q and B bands of porphyrins all orbitals involved in the transitions in question will be taken into account. Equations 3.2 and 3.3 express $\Psi(1E_{1,u}^x)$ and $\Psi(1E_{1,u}^y)$, respectively, in terms of the orbitals involved in the one-electron excitations, Table 3.1.

$$\begin{aligned} \Psi(E_{1,u}^x) = & c_1 \left(\frac{1}{\sqrt{2}} |a_{1,u}^+ e_{1,g}^{x-}| - \frac{1}{\sqrt{2}} |a_{1,u}^- e_{1,g}^{x+}| \right) + c_2 \left(\frac{1}{\sqrt{2}} |2a_{2,u}^+ e_{1,g}^{y-}| - \frac{1}{\sqrt{2}} |2a_{2,u}^- e_{1,g}^{y+}| \right) \\ & + c_3 \left(\frac{1}{\sqrt{2}} |b_{2,u}^+ e_{1,g}^{y-}| - \frac{1}{\sqrt{2}} |b_{2,u}^- e_{1,g}^{y+}| \right) + c_4 \left(\frac{1}{\sqrt{2}} |1a_{2,u}^+ e_{1,g}^{y-}| - \frac{1}{\sqrt{2}} |1a_{2,u}^- e_{1,g}^{y+}| \right) \end{aligned} \quad 3.2$$

$$\begin{aligned} \Psi(E_{1,u}^y) = & c_1 \left(\frac{1}{\sqrt{2}} |a_{1,u}^+ e_{1,g}^{y-}| - \frac{1}{\sqrt{2}} |a_{1,u}^- e_{1,g}^{y+}| \right) - c_2 \left(\frac{1}{\sqrt{2}} |2a_{2,u}^+ e_{1,g}^{x-}| - \frac{1}{\sqrt{2}} |2a_{2,u}^- e_{1,g}^{x+}| \right) \\ & + c_3 \left(\frac{1}{\sqrt{2}} |b_{2,u}^+ e_{1,g}^{x-}| - \frac{1}{\sqrt{2}} |b_{2,u}^- e_{1,g}^{x+}| \right) - c_4 \left(\frac{1}{\sqrt{2}} |1a_{2,u}^+ e_{1,g}^{x-}| - \frac{1}{\sqrt{2}} |1a_{2,u}^- e_{1,g}^{x+}| \right) \end{aligned} \quad 3.3$$

An orbital diagram for MP can be found in Figure 3.1. Two $a_{2,u}$ orbitals are involved and so the prefix 1 and 2 are used to distinguish them as seen in Table 3.1 and Figure 3.1.

Substituting Equations 3.2 and 3.3 into 3.1 affords the general expression 3.4.

$$\frac{A}{D} = -\frac{1}{2} \left[\begin{aligned} &c_1^2 \left(\langle e_{1,g}^{x-} | \hat{L}_z | e_{1,g}^{y-} \rangle + \langle e_{1,g}^{x+} | \hat{L}_z | e_{1,g}^{y+} \rangle \right) - c_2^2 \left(\langle e_{1,g}^{y-} | \hat{L}_z | e_{1,g}^{x-} \rangle + \langle e_{1,g}^{y+} | \hat{L}_z | e_{1,g}^{x+} \rangle \right) \\ &+ c_3^2 \left(\langle e_{1,g}^{y-} | \hat{L}_z | e_{1,g}^{x-} \rangle + \langle e_{1,g}^{y+} | \hat{L}_z | e_{1,g}^{x+} \rangle \right) - c_4^2 \left(\langle e_{1,g}^{y-} | \hat{L}_z | e_{1,g}^{x-} \rangle + \langle e_{1,g}^{y+} | \hat{L}_z | e_{1,g}^{x+} \rangle \right) \\ &- c_1 c_2 \left(\langle a_{1,u}^+ | \hat{L}_z | 2a_{2,u}^+ \rangle + \langle a_{1,u}^- | \hat{L}_z | 2a_{2,u}^- \rangle \right) + c_1 c_2 \left(\langle 2a_{2,u}^+ | \hat{L}_z | a_{1,u}^+ \rangle + \langle 2a_{2,u}^- | \hat{L}_z | a_{1,u}^- \rangle \right) \\ &- c_1 c_4 \left(\langle a_{1,u}^+ | \hat{L}_z | 1a_{2,u}^+ \rangle + \langle a_{1,u}^- | \hat{L}_z | 1a_{2,u}^- \rangle \right) + c_1 c_4 \left(\langle 1a_{2,u}^+ | \hat{L}_z | a_{1,u}^+ \rangle + \langle 1a_{2,u}^- | \hat{L}_z | a_{1,u}^- \rangle \right) \end{aligned} \right] \quad 3.4$$

After finding the diagonal and non-diagonal products and discarding the terms that cancel out, we arrive at the general equation shown below:

$$\begin{aligned} \frac{A}{D} &= - \left((c_1^2 + c_2^2 - c_3^2 + c_4^2) \langle e_g^x | \hat{L}_z | e_g^y \rangle + 2c_1 c_2 \left(- \langle a_{1,u} | \hat{L}_z | 2a_{2,u} \rangle \right) + 2c_1 c_4 \left(- \langle a_{1,u} | \hat{L}_z | 1a_{2,u} \rangle \right) \right) \\ &= T_1 + T_2 + T_3 \end{aligned} \quad 3.5$$

It is possible to further analyze the term A/D by expressing the $e_{1,g}^x$, $e_{1,g}^y$, $a_{1,u}$, and $a_{2,u}$ as a linear combination of atomic orbitals but since it is not vital for the calculation of the MCD parameters it is not shown here.

3.3.3 Detailed Discussion of Simulated MCD spectra for MP based on the A term

For the three porphyrin systems MP ($M=\text{Zn, Mg, Ni}$) we find positive A - and A/D terms for the Q band, Table 3.1. This is in agreement with the available experimental data limited to ZnP. Thus Keegan et al. [77] report a value of $4.2 \mu_B$ for A/D which is in reasonable agreement with our estimate of $5.46 \mu_B$. We note again that the experimental MCD spectrum for ZnP exhibits two A -terms in the Q -band region, Figure 3.8, due to vibronic coupling, whereas only one positive A -band is present in our simulation where vibronic coupling is neglected. Also note that the simulated MCD spectra in Figure 3.9 only contain contributions from the A terms.

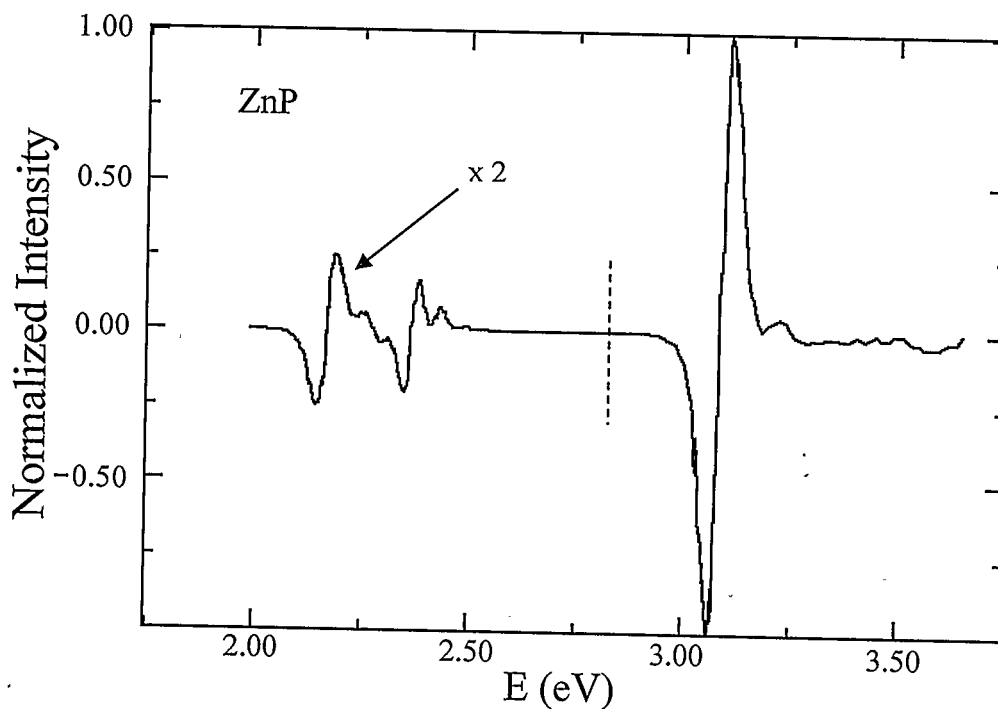


Figure 3.8. Experimental MCD spectrum for ZnP [73].

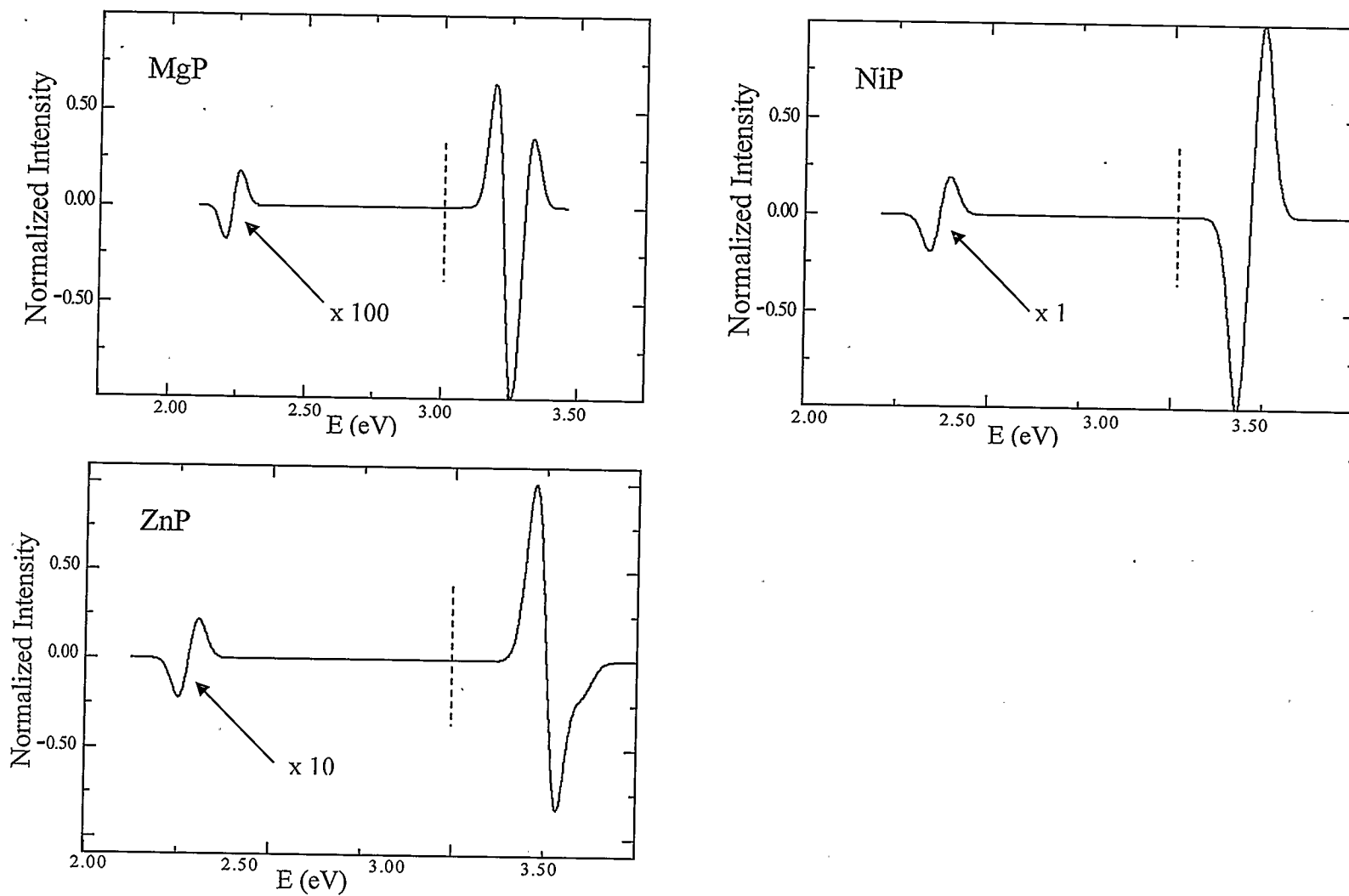


Figure 3.9. Simulated MCD spectra of MP based on A terms alone where $M=\{\text{Mg, Ni, Zn}\}$.

Table 3.2. Some of the relevant integrals used to calculate the A/D term for the Q and B bands of MP.

	Zn	Mg	Ni
$\langle e_{1,g}^x \hat{L}_z e_{1,g}^y \rangle^1$	-2.872	-2.881	-2.810
$\langle a_{1,u} \bar{L}_z 2a_{2,u} \rangle^1$	2.616	2.587	2.651

¹Integrals expressed in μ_B .

The excited state ($1E_{1,u}$) representing the Q band can in agreement with the 4 orbital model of Gouterman [49-55], be described by the wave function in Equations 3.2 and 3.3 where $c_1 \sim c_2 \sim \frac{1}{\sqrt{2}}$ whereas $c_3 = c_4 = 0$. As a consequence, only the first two terms ($T_1 + T_2$) in Equation 3.5 will contribute to the numerical value of A/D . The term $T_1 = -(c_1^2 + c_2^2 - c_3^2 + c_4^2) \langle e_g^x | \hat{L}_z | e_g^y \rangle$ will contribute with a positive value since $\langle e_g^x | \hat{L}_z | e_g^y \rangle$ is negative, Table 3.2. The contribution from $T_2 = 2c_1c_2 \langle a_{1,u} | \hat{L}_z | 2a_{2,u} \rangle$ is also positive due to the positive sign of $\langle a_{1,u} | \bar{L}_z | 2a_{2,u} \rangle$.

Turning next to the Soret band, we note that in Gouterman's model $c_1 = -c_2 = \frac{1}{\sqrt{2}}$ for the second conjugated state ($2E_{1,u}$). As a consequence of Equation 3.5 a small value of A/D would be predicted as $\langle e_g^x | \hat{L}_z | e_g^y \rangle$ numerically is larger than $\langle a_{1,u} | \bar{L}_z | 2a_{2,u} \rangle$, see Table 3.2, and T_1 and T_2 are of opposite sign. Gouterman's model applies approximately to NiP, Table 3.1, where we find one A term in the Soret region due to the conjugated excited state, $c_1 \square -c_2 = \frac{1}{\sqrt{2}}$, with a small positive A/D term of $0.31 \mu_B$ and an A term of $8.9 D^2 \mu_B$ at the absorption energy 3.21 eV. At slightly higher energy (3.41 eV) another excited

state of $E_{1,u}$ symmetry ($3E_{1,u}$) is found for NiP and it is entirely due to a $1b_{2,u} \rightarrow 2e_{1,g}$ one-electron transition, Table 3.1. This transition has an A/D value of $-2.75 \mu_B$ and a neglectable A -term of $-0.65 \times 10^{-3} D^2 \mu_B$. Thus the simulated MCD spectrum of NiP in Figure 3.9b based only on the A term exhibits a single band with a positive A/D term in the Soret region. Applying the Gouterman's model to $2E_{1,u}$ of MgP and ZnP with $c_1 = -c_2 = \frac{1}{\sqrt{2}}$ in the Soret region would also lead to one A -term in the Soret region with a small positive A/D value if use is made of the $\langle e_g^x | \hat{L}_z | e_g^y \rangle$, $\langle a_{1,u} | \bar{L}_z | 2a_{2,u} \rangle$ and $\langle a_{1,u} | \bar{L}_z | 1a_{2,u} \rangle$ values reported in Tables 3.2. Likewise a transition of higher energy involving the $1b_{2,u} \rightarrow 2e_{1,g}$ one-electron excitation ($3E_{1,u}$) would lead to a weak band with a small A -term ($\sim 10^{-3}$). Such a picture is not in agreement with the experimental observation since the recorded MCD spectrum, Figure 3.9, exhibits a single positive A -like term in the Soret band region.

In our calculations the conjugated second Gouterman excited state $2E_{1,u}$ with $\left(c_1 = -c_2 = \frac{1}{\sqrt{2}} \right)$ is very close to $3E_{1,u}$ ($1b_{2,u} \rightarrow 2e_{1,g}$, $c_3 \cong 1$) with the result that $2E_{1,u}$ and $3E_{1,u}$ mix. The mixing gives rise to a complex A term only MCD spectrum with a negative A -term followed by a positive A -term in the Soret region of MgP, Figure 3.9, and two negative A -term in the Soret band region in the case of ZnP, Figure 3.9. The simulated spectrum for ZnP based on A terms alone does not agree with the recorded MCD spectrum for ZnP.

3.3.4 Influence of Porphyrin Ring Distortions on the Simulated MCD Spectrum

It has been reported that symmetry distortions of the porphyrin ring can have a considerable influence on the MCD spectrum [16]. We have as a consequence considered whether bending (by 10°) of the porphyrin ring along one of the N-M-N axis in any way should improve the agreement between the recorded and simulated spectrum for ZnP. A bend of the ring will reduce the symmetry of ZnP to C_{2v} and split the three n^1E_u ($n=1,3$) excited states into three nearly degenerate pairs ($n^1B_1, n^1B_2; n=1,3$) with an energy separation for each pair of $\Delta W_n = W(n^1B_2) - W(n^1B_1)$. In planar ZnP the A term for each of the three excited states comes from the mixing of the n^1E_{ux} and n^1E_{uy} components. In the bent ZnP we describe the same phenomenon by allowing the magnetic field to mix the n^1B_1, n^1B_2 components with the same n . We thus get, according to the theory outlined in the previous chapter for each $n=1, 3$, two B -terms

$$B(n^1B_1) = 2mC \cdot \frac{\langle n^1B_1 | \tilde{L}_z | n^1B_2 \rangle \langle {}^1A_1 | \mu_x | n^1B_1 \rangle \langle n^1B_2 | \mu_y | {}^1A_1 \rangle}{\Delta W_n} \quad 3.6a$$

and

$$B(n^1B_2) = -2mC \cdot \frac{\langle n^1B_1 | \tilde{L}_z | n^1B_2 \rangle \langle {}^1A_1 | \mu_x | n^1B_1 \rangle \langle n^1B_2 | \mu_y | {}^1A_1 \rangle}{\Delta W_n} \quad 3.6b$$

that are equal in size but opposite in sign and separated by ΔW_n . They will thus appear in the MCD spectrum as pseudo A -terms [78]. Figure 3.10 presents the simulated MCD spectrum based on the three pseudo A -terms. It is clear from a comparison of Figure 3.9c and Figure 3.10 that the bend only has a minor influence. Calculations with other values for the bending angle led to a similar conclusion.

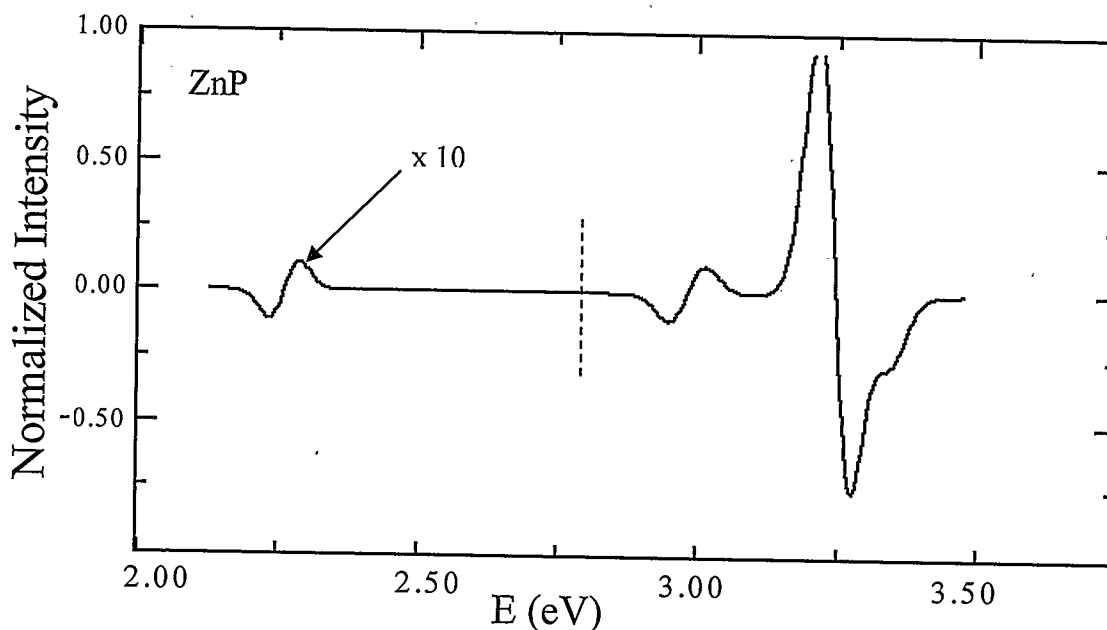


Figure 3.10. Pseudo- A terms calculated after applying a small geometric perturbation to the ZnP molecule.

3.3.5 Influence of B Terms on the Simulated MCD Spectra of Planar MP

So far we have neglected the magnetic coupling between excited states n^1E_u and p^1E_u where n is different from p which gives rise to the B -terms discussed in Chapter 2.

We get for each of the three excited states n^1E_u ($n=1,3$) an associated B term given by

$$\mathcal{B}(nE_{1,u}) = 4\mathcal{S}_m C \sum_{p=1, p \neq n} \frac{\langle nE_{1,ux} | \hat{L} | pE_{1,uy} \rangle}{W(pE_{1,uy}) - W(nE_{1,ux})} \cdot \left(\langle A_{1,g} | \mu_x | nE_{1,ux} \rangle \langle pE_{1,uy} | \mu_y | A_{1,g} \rangle \right) \quad 3.7$$

Figure 3.11 displays the simulated spectrum due to the B -terms given in Equation 3.7 for all three MP systems. The B term for $n = 1$ in the Q -band is very small due to the large separation between 1^1E_u on the one hand and 2^1E_u and 3^1E_u on the other, see Table 3.1. However the B -terms for 2^1E_u and 3^1E_u in the Soret region are numerically large and of opposite sign as they are dominated by the magnetic coupling of 2^1E_u and 3^1E_u due to the small energy separation between the two states. The fact that they are of opposite sign and close in energy makes them appear as one “pseudo” A -term. The numerical calculation further shows that this “pseudo” A -term is positive.

When we finally add the A -terms of Figure 3.9 to the B -terms of Figure 3.11 we get in Figure 3.12 a fully simulated MCD spectrum that is quite similar for the 3 systems and in qualitatively good agreement with experiment for ZnP, Figure 3.12. Thus, we now have one dominating positive “pseudo” A -term due to the magnetic coupling between 2^1E_u and 3^1E_u in the Soret band region.

3.3.6 Detailed Discussion of Simulated MCD Spectra for MTPP Based on the A Term

The simulated MCD spectra for the Q band of the MTPP systems (M =Mg, Ni, Zn) based on the A term alone are very similar to the corresponding spectra for the pure porphyrins, MP, Figures 3.9 and 3.13. Thus both MTPP and MP exhibit a positive A -term

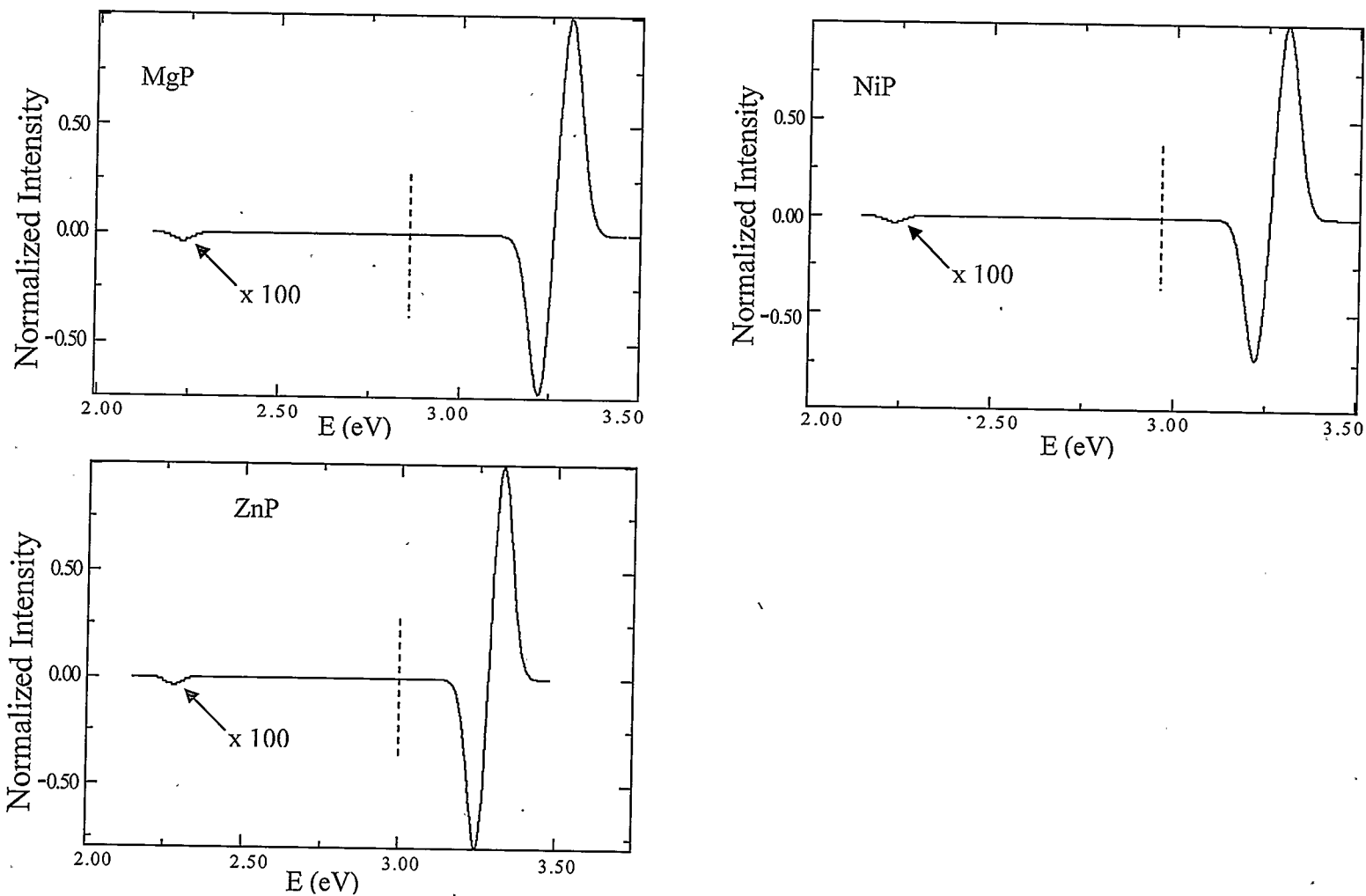


Figure 3.11 Simulated MCD including only the B terms due to the mixing of different excited states for the MP systems.

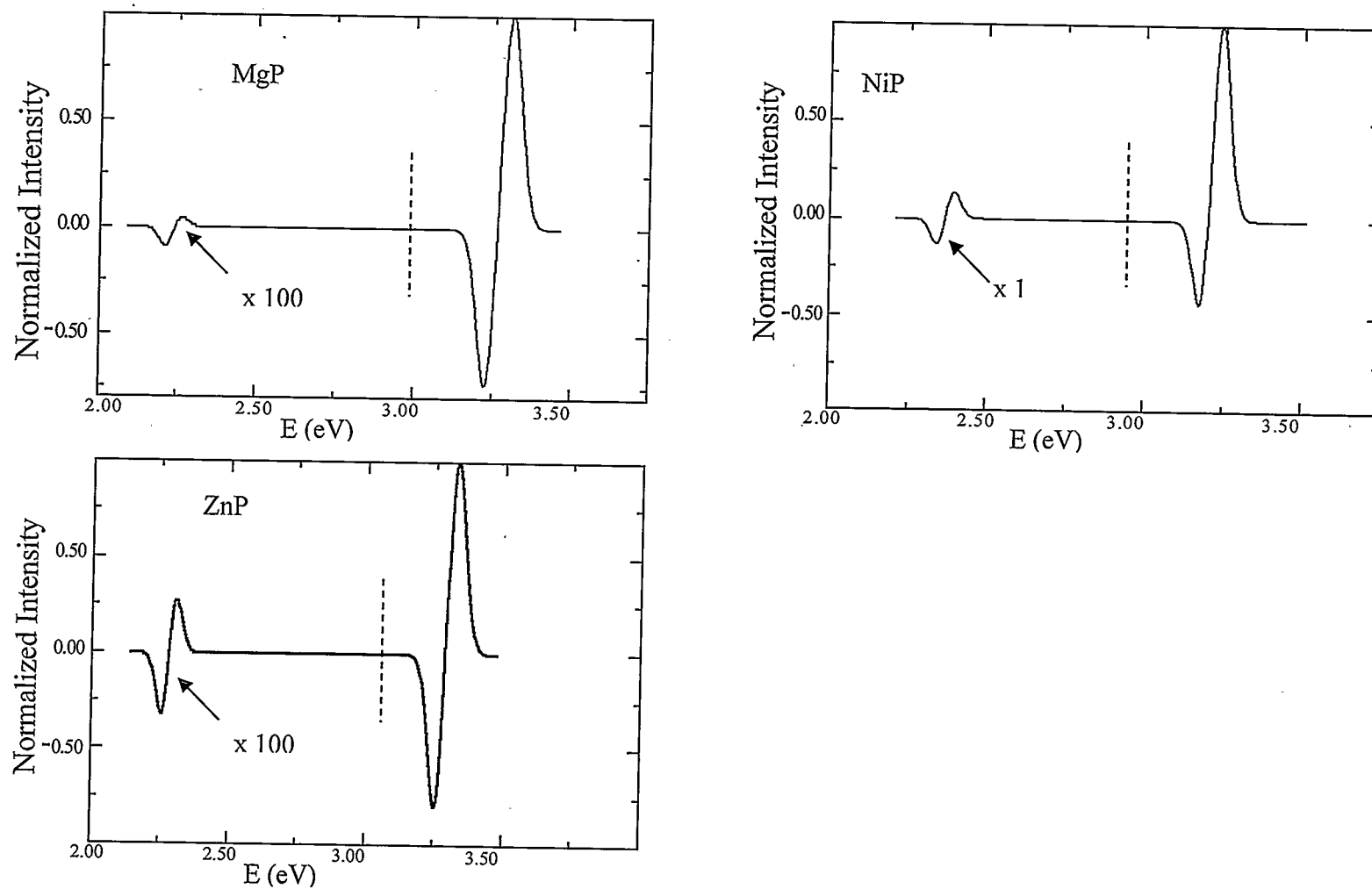


Figure 3.12. MCD spectra of MP complexes including both A and B terms.

with comparable A/D values, Tables 3.1, 3.3. This is in agreement with experimental data available for NiTPP [70] and ZnTPP [77, 80], Figures 3.14 and 3.15. Keegan et al. [77] reported a value of $3.52 \mu_B$ for A/D of ZnTPP compared to the theoretical estimate of $5.17 \mu_B$. Although the agreement is reasonable, the calculated value appears to be overestimated. It should be noted that, as in the case of MP, two A -terms are observed experimentally in the Q band MCD spectra of ZnTPP and NiTPP, Figures 3.14 and 3.15. We highlight again that the two experimental A -terms are due to vibronic coupling. Our simulation neglects at the moment vibronic coupling and we find for that reason only a single (positive) A -term in the Q -band region. We should note that the experimental MCD spectrum used for comparison corresponds to NiOETPP where an additional ethyl group was added in the β positions besides the phenyl groups addition in the m positions.

As for the MP systems, the first excited state ($1E_{1,u}$) in MTPP responsible for the observation of the Q band can be described by the wave function in Equation 3.2 and (3.3) with $c_1 \sim c_2 \sim \frac{1}{\sqrt{2}}$ in accordance with the Gouterman's 4-orbital model [49-55].

Since $c_3 = c_4 = 0$ only the first two terms, T_1 and T_2 , will contribute to the final value of A/D . The contribution from T_1 to A/D is positive since it can only be affected by the sign of the integral $\langle e_g^x | \hat{L}_z | e_g^y \rangle$, which is negative. T_2 also contributes with a positive sign since the sign of $\langle a_{1,u} | \tilde{L}_z | 2a_{2,u} \rangle$ as well as the coefficients in T_2 are positive, Table 3.4.

Applying the Gouterman model to the Soret region of the MTPP systems would give

$c_1 = -c_2 = \frac{1}{\sqrt{2}}$ and $c_3 = c_4 = 0$. The use of the Gouterman model gives rise to an intense

absorption at the $2E_{l,u}$ state of NiTPP with $f=2.98$ and yields a positive A -term of $2.19 D^2\mu_B$ in the Soret region, Figure 3.13 with a small positive A/D term of $0.33 \mu_B$ at the absorption energy of 3.03 eV , Table 3.3. The calculated positive A -term in the Soret region (Figure 3.13) is in good agreement with experiment where only a single A term is observed, (Figure. 3.14, [70]). An additional state ($3E_{l,u}$) is calculated at a higher energy (3.28 eV). It is due mainly to the one-electron transition $1b_{2,u} \rightarrow 2e_{1,g}$, Table 3.3. This transition has a negative A -term with $A = -0.18 D^2\mu_B$ and $A/D = -2.64 \mu_B$, Table 3.3, just as the corresponding transition to $3E_{l,u}$ in NiP, Table 3.2. The simulated MCD spectrum for NiTPP based on A -terms alone reveals, in agreement with experiment, only a single positive A -term as the numerically much smaller negative A -term from $3E_{l,u}$ is hidden under the large positive A -term for $2E_{l,u}$. For nickel we calculate in addition a ligand to metal charge transfer transition corresponding to the $1e_{l,u} \rightarrow d_{x^2-y^2}$ excitation at 3.16 eV . We do not count this transition in our numbering of $nE_{l,u}$ state for the sake of comparison with ZnTPP and MgTPP where it is absent. The $1e_{l,u} \rightarrow d_{x^2-y^2}$ transition has a modest absorption intensity ($f=0.104$) with a small A -term ($A = 0.02 D^2\mu_B$; $A/D = 0.09 \mu_B$) that is buried under the main $2E_{l,u}$ band in the simulated MCD spectrum of NiTPP.

For MgTPP and ZnTPP we find again that the calculated transition of lowest energy in the Soret region is assigned to the conjugated Gouterman state $2E_{l,u}$ ($c_1 = -c_2$), Table 3.3. However, some mixture is observed with the one-electron

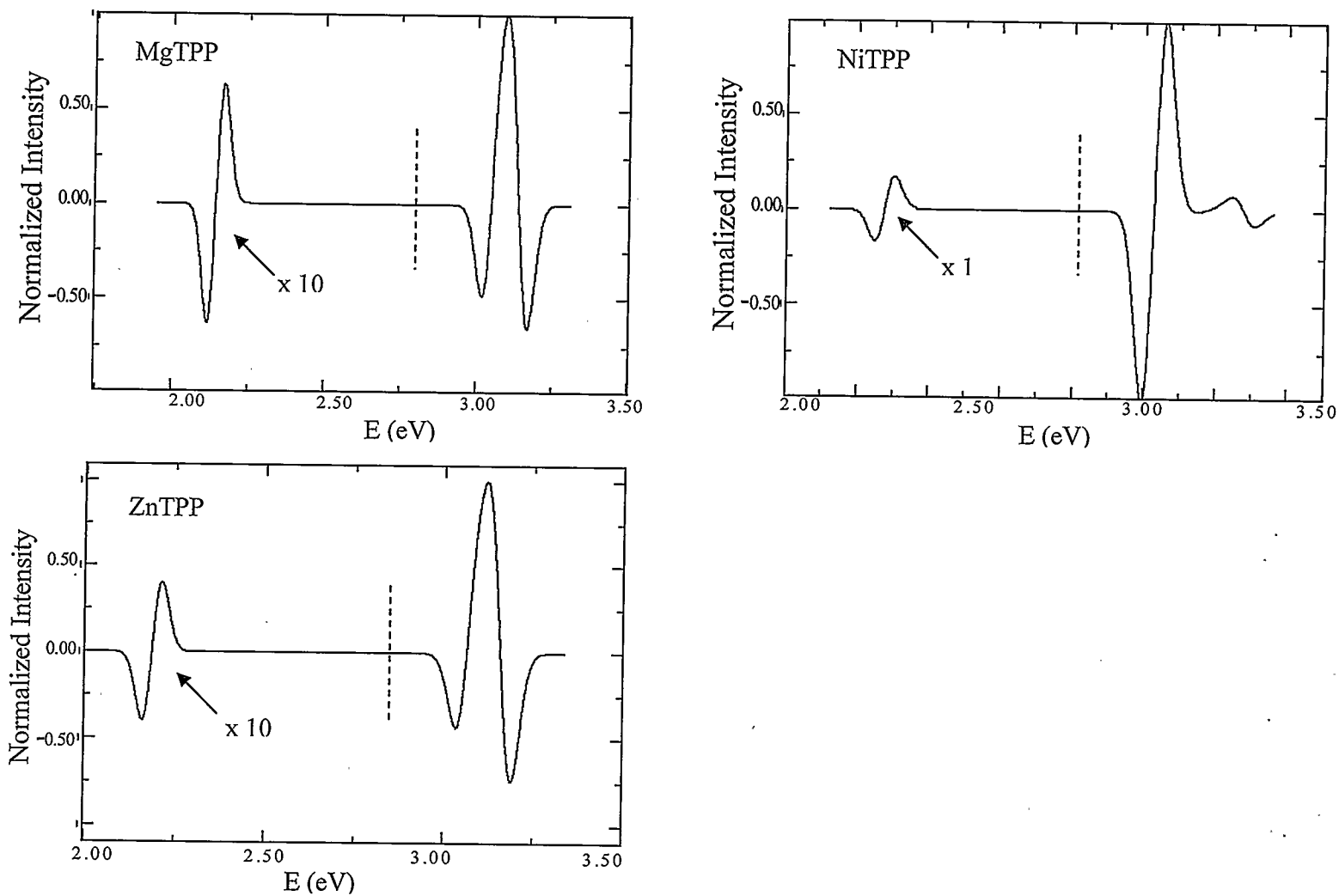


Figure 3.13 Simulated MCD spectrum of MTPP based on A terms alone.

Table 3.3. Calculated excitation energies (eV), oscillator strength (f), A, A/D, B and B/D terms for MTPP (M=Mg, Ni, Zn).

Complex	Symmetry	Exc. Energ. (eV)		Composition	%	f	A ($D^2\mu_B$)	A/D (μ_B)	B	B/D	Assign.
		exp.	calc.								
MgTPP	E_u		2.14	2a2.u → 2e1.g 1a1.u → 2e1.g	58.00 40.81	0.014	0.23	5.14	17.42	0.38×10^{-3}	Q
				1a1.u → 2e1.g 2a2.u → 2e1.g 1b2.u → 2e1.g	43.24 26.35 17.09	3.302	2.58	0.36	-2.23×10^3	-0.31×10^3	B
	E_u		3.05								
				1b2.u → 2e1.g 2a2.u → 2e1.g 1a1.u → 2e1.g	80.41 7.73 5.80	0.754	-3.55	-2.17	3.01×10^3	1.84×10^3	
			3.14								
	E_u	1.98 ^a	2.28	2a2.u → 2e1.g 1a1.u → 2e1.g	52.06 46.82	0.901×10^{-4}	2.79×10^{-3}	5.18	0.81	1.50×10^{-3}	Q
NiTPP	$A_{2,u}$		2.89	1b2.u → dx^2-y^2	99.77	0.781×10^{-4}	0.00	0.00	-0.44	-1.20×10^{-3}	
	E_u	2.91 ^a	3.03	1a1.u → 2e1.g 2a2.u → 2e1.g	44.35 38.78	2.9804	2.19	0.33	53.07	7.92	B
				1e1.u → dx^2-y^2	96.17	0.104	0.02	0.09	0.64	2.87	
	E_u		3.16								
ZnTPP	E_u		3.28	1b2.u → 2e1.g	95.09	0.034	-0.18	-2.64	19.58	0.28×10^3	
	E_u	2.05 ^b , 2.16 ^c	2.19	2a2.u → 2e1.g 1a1.u → 2e1.g	55.94 42.86	0.008	0.12	5.17	10.20	0.41	Q
				1a1.u → 2e1.g 2a2.u → 2e1.g 1b2.u → 2e1.g	43.66 29.56 15.05	3.352	1.94	0.26	-1.92×10^3	-0.26×10^3	B
	E_u	2.97 ^b , 2.89 ^c	3.07								
				1b2.u → 2e1.g	82.32	0.708	-3.41	-2.24	2.54×10^3	1.67×10^3	

	2a2.u	-> 2e1.g	7.52
	1a1.u	-> 2e1.g	4.99
^a Ref 79, ^b Ref 77, ^c Ref 70			

Table 3.4. Some of the relevant integrals used to calculate the A/D term for the *Q* and *B* bands of MTPP.

	Zn	Mg	Ni
$\langle e_{1.g}^x \hat{L}_z e_{1.g}^y \rangle^1$	-2.758	-2.767	-2.490
$\langle a_{1.u} \tilde{L}_z 2a_{2.u} \rangle^1$	2.454	2.430	-2.702

¹Integrals expressed in μB .

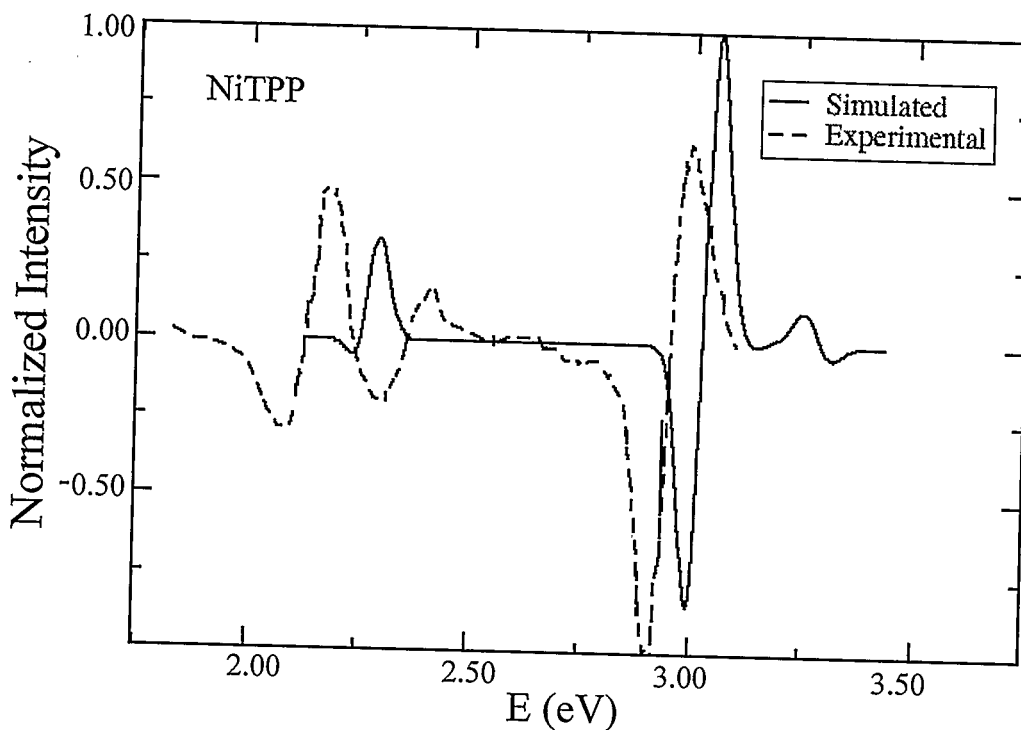


Figure 3.14 Experimental and simulated MCD spectra of NiTPP [70].

transition $1b_{2,u} \rightarrow 2e_{1,g}$ ($c_3 = 0.5$). In spite of this admixture, $2E_{1,u}$ for MgTPP and ZnTPP exhibits similar positive A/D and A values to those obtained for $2E_{1,u}$ of NiTPP, Table 3.3. The second transition in the Soret band corresponds as for NiTPP to the $3E_{1,u}$ state and is primarily made up of the $1b_{2,u} \rightarrow 2e_{1,g}$ transition with some admixture from the conjugated Gouterman state. The A/D term corresponding to $3E_{1,u}$ is negative for MgTPP ($-2.17 \mu_B$) and ZnTPP ($-2.24 \mu_B$) and very similar to NiTPP ($-2.64 \mu_B$) although slightly reduced numerically. However, the A -terms for MgTPP ($-3.55 D^2 \mu_B$) and ZnTPP ($-3.41 D^2 \mu_B$) are numerically much larger than for NiTPP ($-0.18 D^2 \mu_B$). The reason for that is the larger f value for MgTPP (0.754) and ZnTPP (0.708) compared to NiTPP (0.034) as the result of the admixture of the conjugated Gouterman state into

$3E_{1,u}$. The experimental MCD spectrum of ZnTPP exhibits as in the case of NiTPP a positive A -band in the Soret region which we might attribute to $2E_{1,u}$, Figure 3.15. However, the experimental MCD spectrum does not reveal a second negative A -term for ZnTPP as predicted computationally. We shall address this discrepancy in the next section where we discuss the influence from the B -term on the MCD spectrum.

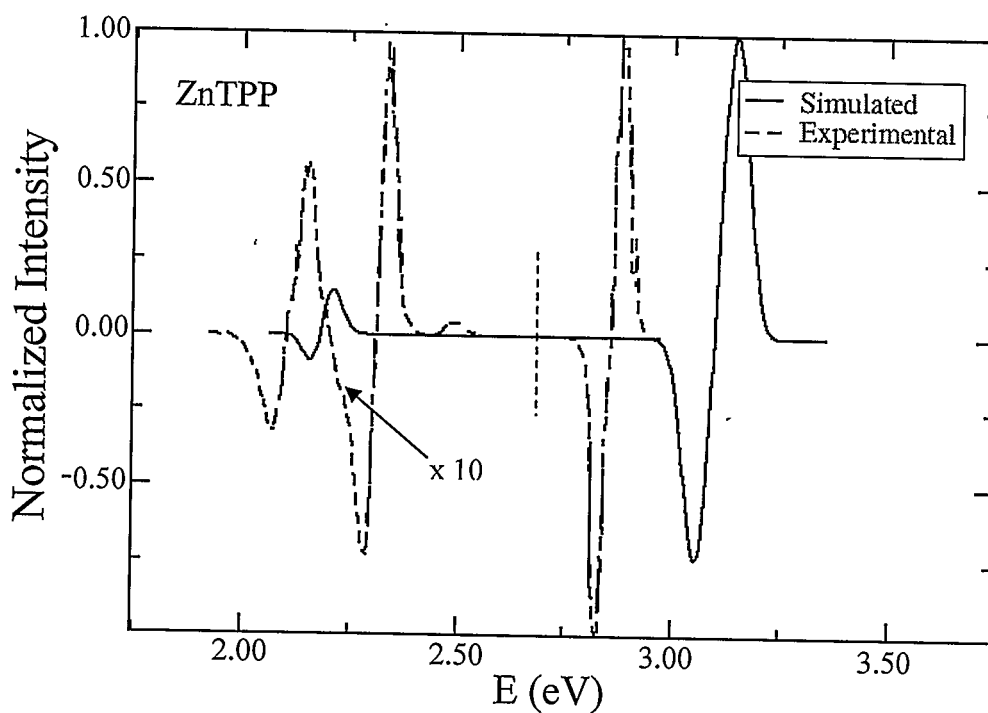


Figure 3.15 Comparison of experimental [77] and simulated MCD spectrum for ZnTPP.

3.3.7 Influence of B Terms in the MCD Spectra of MTPP

It follows from our discussion of the MP systems that it is important to include the B -term into the simulation in order to obtain good agreement with experiment. We shall thus discuss here the influence of the B term on the simulated MCD spectra of the

MTPP systems (M=Mg, Ni, Zn). The expression for the B term due to the coupling between different excited states n^1E_u and p^1E_u by the magnetic field is given in Equation 3.7.

As for the porphyrin complexes, the B -term in the Q band region of MTPP is small due to the large separation between the 1^1E_u state and other states of E_u symmetry, Figure 3.16. Thus, the Q -band region for the simulated MCD spectra of MTPP will be determined by the A -terms, Figure 3.17. For NiTPP we find only modest B -terms for 2^1E_u (3.03 eV) and 3^1E_u (3.28 eV) as the two states are relatively well separated (~ 0.25 eV), Figure 3.16. The simulated MCD spectrum for NiTPP is as a consequence dominated in the Soret region by a single positive A term (Figure 3.17) in agreement with experiment, Figure 3.14.

The B -terms in the Soret region for 2^1E_u and 3^1E_u are much larger (and of opposite sign) in the case of MgTPP and ZnTPP compared to NiTPP as the energy separation between 2^1E_u and 3^1E_u is smaller for $M=\{Mg, Zn\}$ compared to $M=Ni$. The complex MCD spectra of MTPP (M=Mg, Zn) due to the A term of one positive A -band followed by one negative A -band (Figure 3.13) is as a consequence overwritten by two B -terms of opposite sign (Figure 3.16) so that the total simulated MCD spectra appear to have a single positive pseudo- A term, Figure. 3.17, in agreement with experiment, Figure 3.15.

3.3.8 Detailed Discussion of Simulated MCD Spectra for MOEP

The MOEP systems can have D_{4h} symmetry only if the ethyl chains are in the molecular plane as shown in Figure 3.18a. However, such a structure would be strained. We have instead adopted a structure of D_{2d} symmetry with the ethyl chains perpendicular to the molecular plane as shown in Figure 3.18b. However, we shall in spite of the use of a lower symmetry still designate our orbitals according to D_{4h} symmetry. This is justified since the π -ring orbitals look quite similar in the two symmetries.

The Q band of the simulated MCD spectra of MOEP (M=Mg, Ni, Zn) is found to be very similar to the previous discussed systems (MP and MTPP), Figures 3.9, 3.13, 3.19. Therefore, MOEP exhibits a positive A term and very similar A/D values, Tables 3.1, 3.3, 3.5. This is in agreement with experimental data available for NiOEP [70, 79] and ZnOEP [78], Figures 3.20 and 3.21. The experimental MCD spectra of NiOEP have ethyl groups substituted at the m positions besides the octaethyl substitution. We can observe again two bands in the Q region for the NiOEP in the experimental MCD spectrum [79], this can be attributed, as with MP and MTPP, to vibronic coupling. It would be of interest to highlight that, although observed for the NiOEP, this vibronic coupling is barely, if at all, observed in the experimental MCD of ZnOEP [78]. Our calculations predict, as in the previously discussed systems, only one positive A term in the Q -band region.

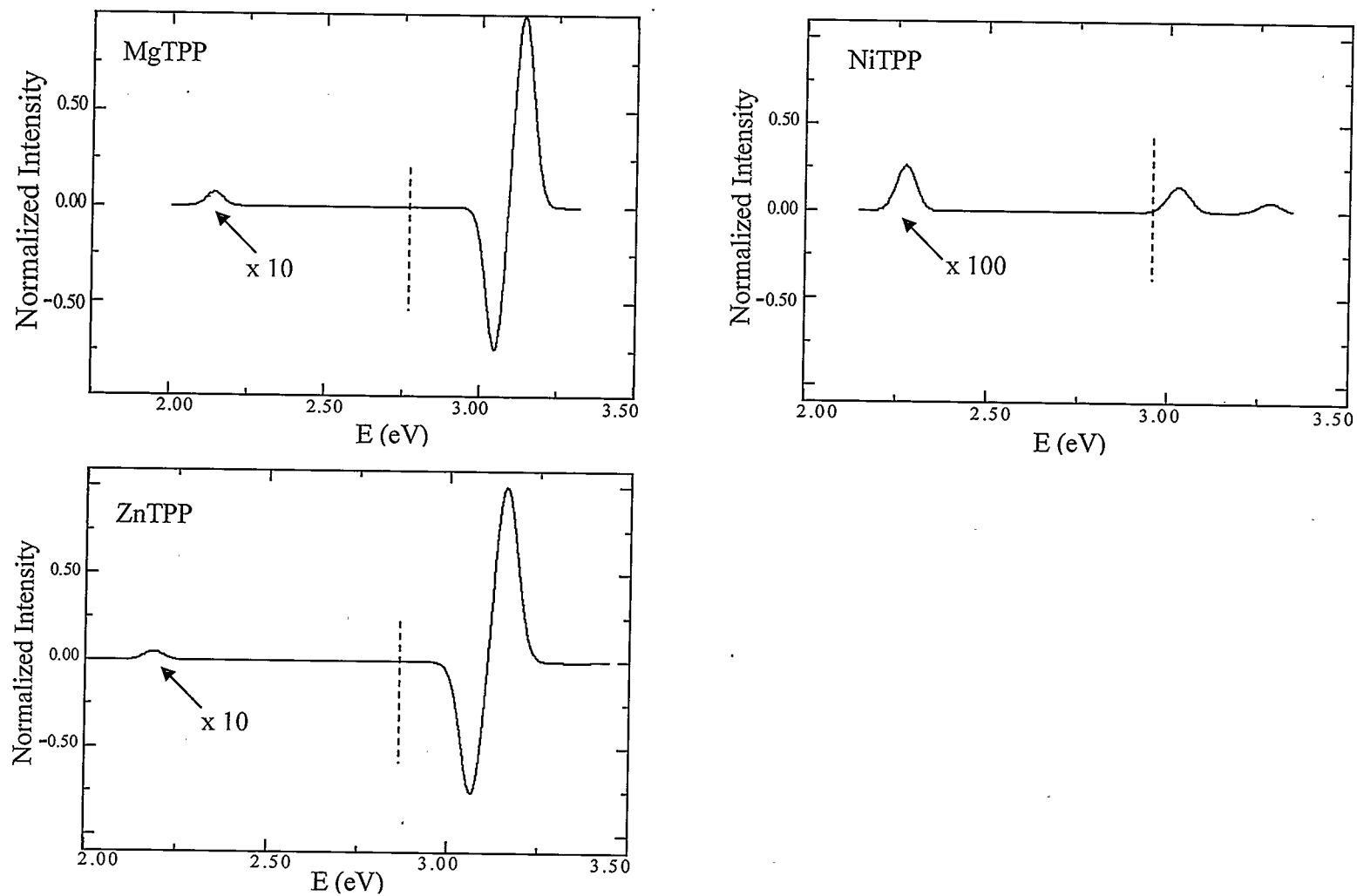


Figure.3.16. Simulated MCD spectra including only B terms for MTPP.

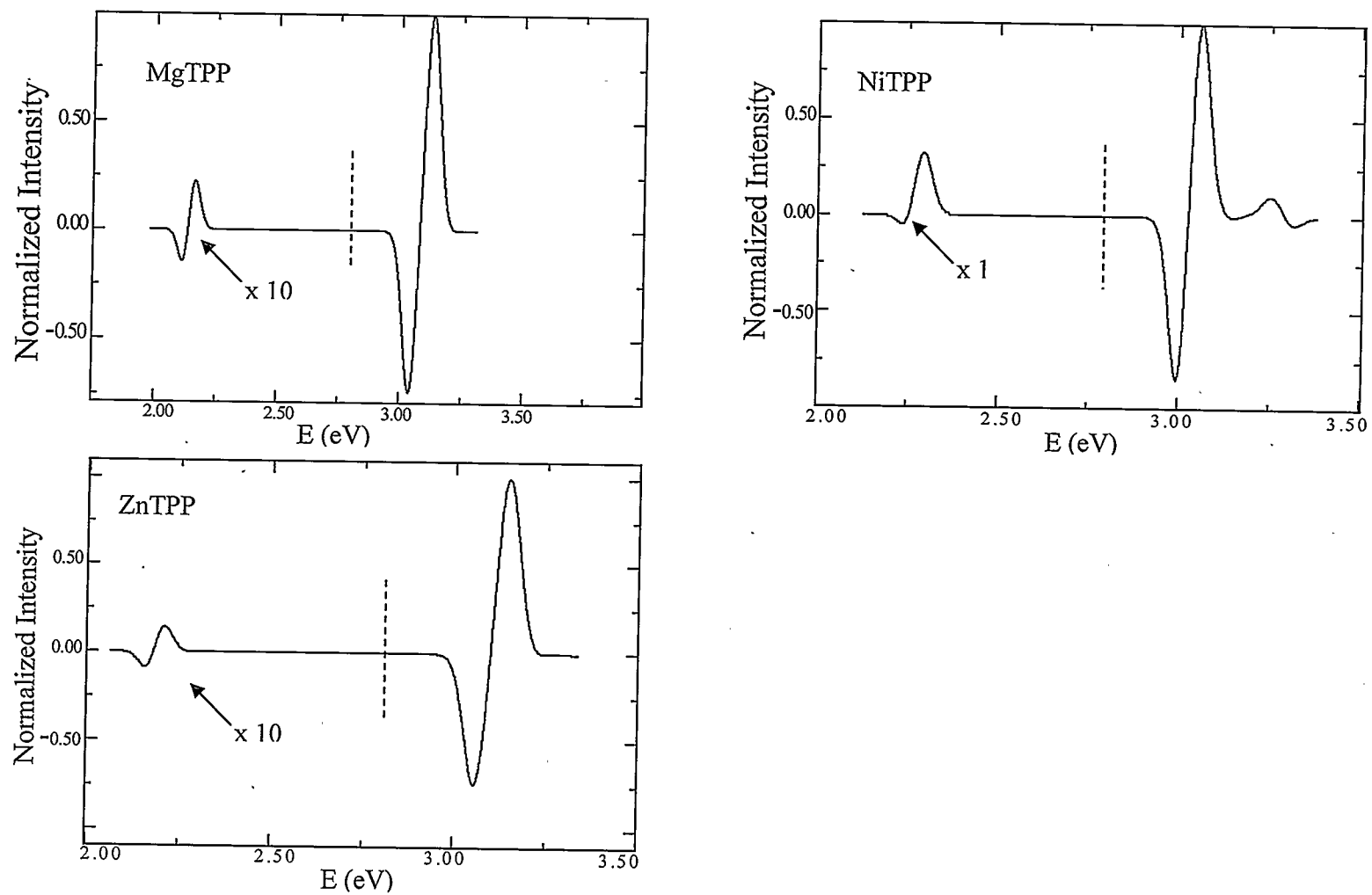


Figure 3.17. Simulated MCD spectra including both A and B terms for MTPP.

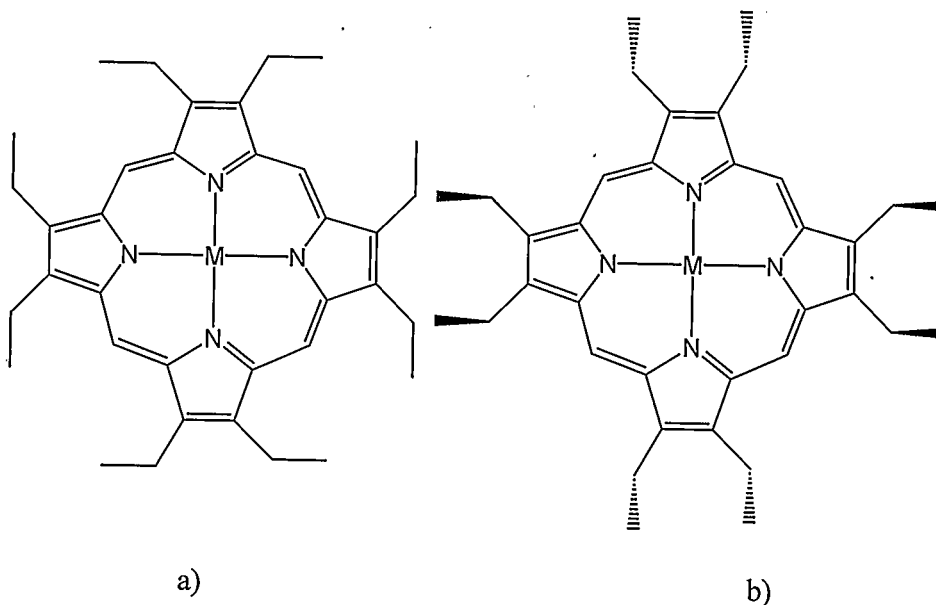


Figure 3.18 Schematic representation of the octaethylporphyrin complexes using a) D_{4h} symmetry and b) D_{2d} symmetry (M = Mg, Ni and Zn).

The observation of the Q band is then possible only in the presence of the first excited state ($1E1_u$) as seen before for ML (L=P, TPP) and can be described using the wave function in Equation 3.2 and 3.3 and using $c_1 = c_2 = \frac{1}{\sqrt{2}}$ in agreement with Gouterman's 4-orbital model [49-55]. Thus the sign of A/D of all previous and current systems is only due to the first terms T_1 and T_2 since $c_3 = c_4 = 0$. The integral $\langle e_g^x | \hat{L}_z | e_g^y \rangle$ is negative so the final contribution of T_1 to the sign of A/D will be positive. The integral $\langle a_{1,u} | \tilde{L}_z | 2a_{2,u} \rangle$ is positive and considering the sign of the coefficients, will result in a positive T_2 and thus contribute with a positive sign to A/D , Table 3.6.

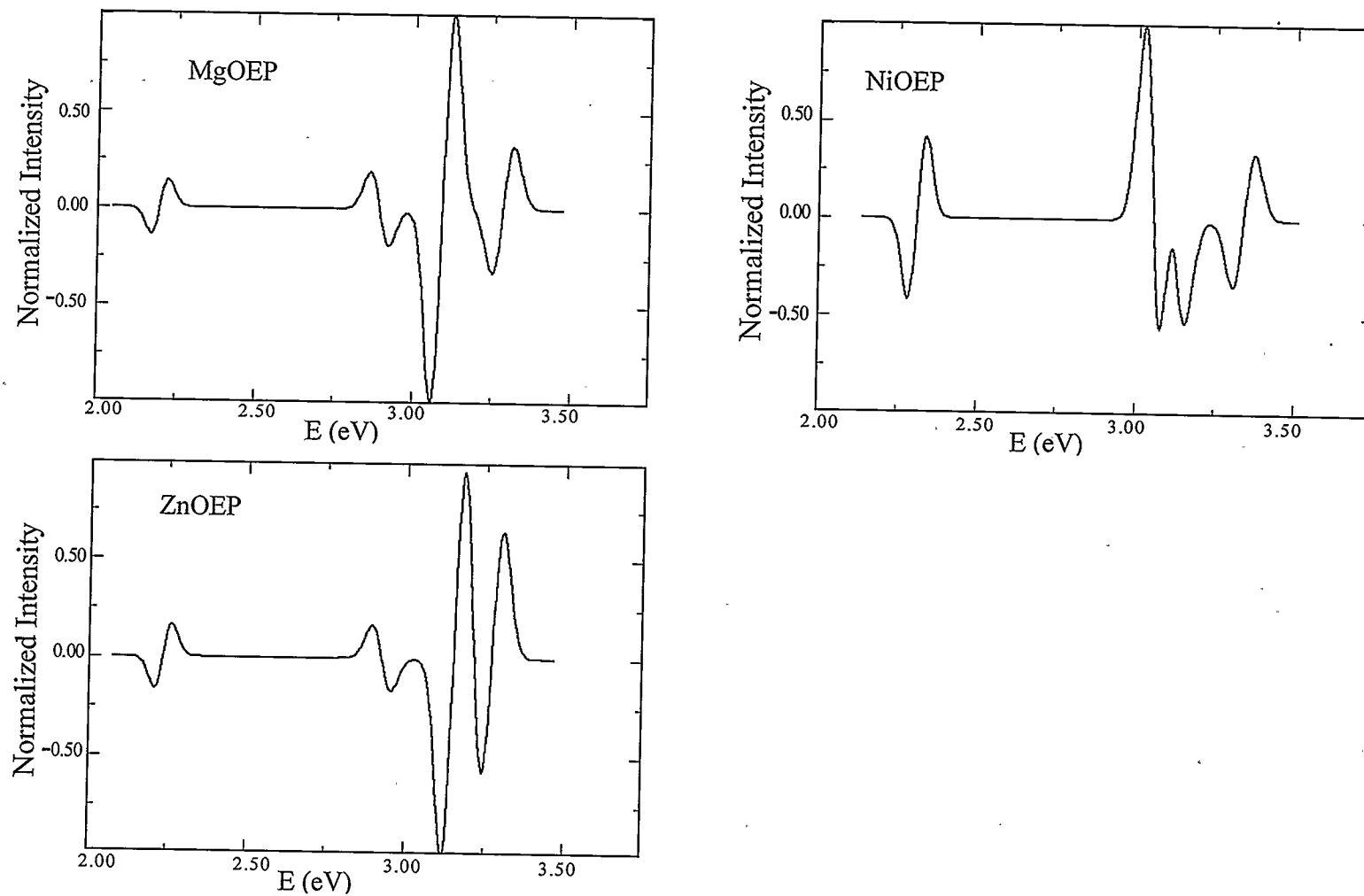


Figure 3.19 Simulated MCD spectrum of MOEP based on A terms alone.

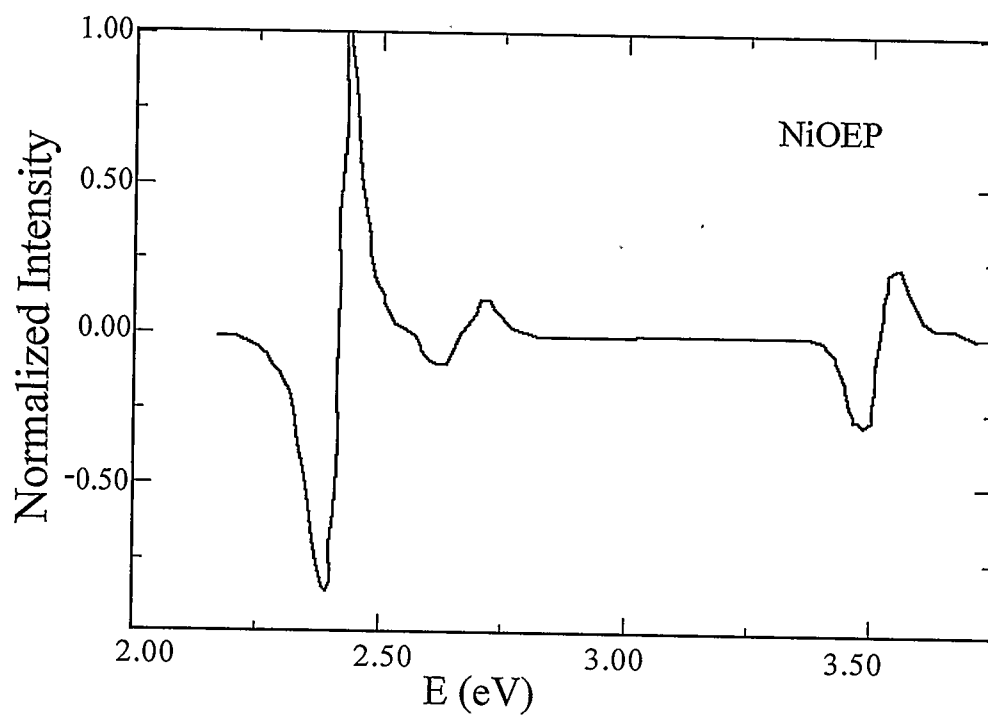


Figure 3.20. Experimental MCD spectrum for NiOEP [70].

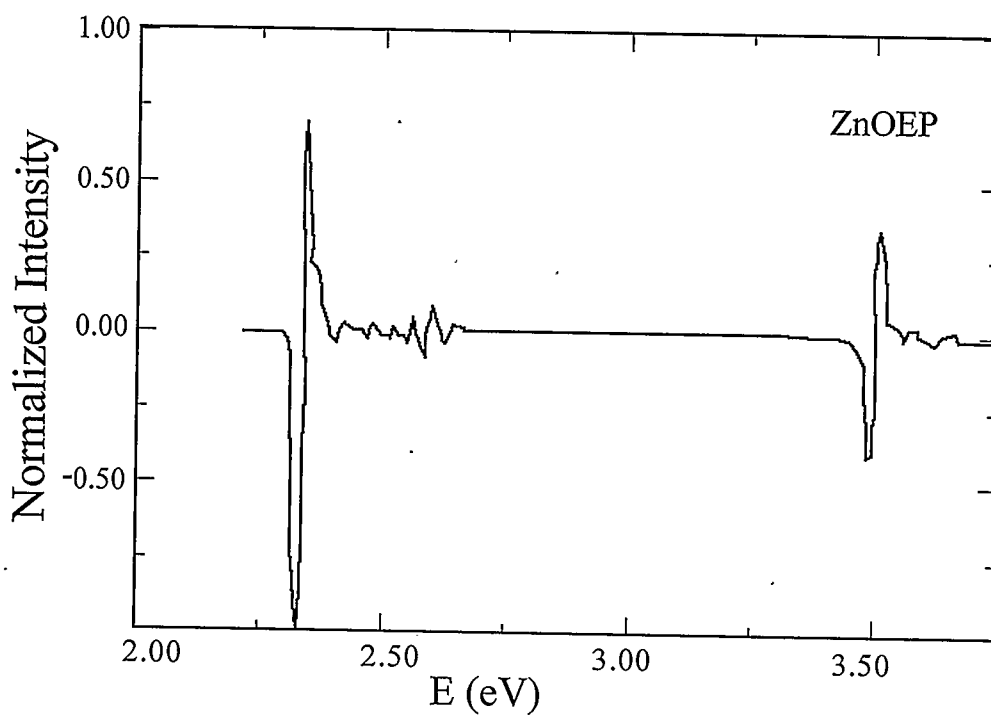


Figure 3.21. Experimental MCD spectrum for ZnOEP [78].

Turning now to the Soret region, we find for NiOEP two excitations with significant absorptions corresponding to $A_{1g} \rightarrow 4E_u$ at 3.05 eV ($f=0.366$) and $A_{1g} \rightarrow 5E_u$ at 3.12 eV ($f=0.920$). The latter can be assigned to the intense transition observed at 3.22 eV, Table 3.5. The $4E_u$ state is primarily represented by the $1b_{2u} \rightarrow 2e_g$ one-electron transition with some mixing from the conjugated Gouterman state, just as we have seen it for a number of MP and MTPP complexes. As in these cases, $4E_u$ exhibits a negative A -term and an intense negative B -term from the magnetic interaction with $5E_u$, Figures 3.19 and 3.22. When A and B -terms are combined, $4E_u$ is dominated by the negative B -term, Figures 3.23. The $5E_u$ state corresponds to the conjugated Gouterman state. It has a positive A -term and a positive B -term from the magnetic interaction with $4E_u$, Figures 3.19 and 3.22. When the A and B -terms are combined, $5E_u$ is dominated by the positive B -term, Figure 3.23. It is clear from the discussion that the simulated MCD spectrum in the Soret region is dominated by a negative B -term due to $4E_u$ followed by a positive B -term due to $5E_u$. The two B -terms combined have the appearance of a positive A -term in agreement with the experimental [79] MCD spectrum for NiOEP, Figure 3.20.

Complex	Symmetry	Exc. Energ.		Composition	%	f	A ($D^2\mu_B$)	A/D (μ_B)	B	B/D	Assign.
		exp.	calc.								
MgOEP	1E _u		2.20	1a1u → 2eg	50.83	0.013	0.42	5.29	9.05	0.11 X 10 ³	Q
				2a2u → 2eg	47.76						
	2E _u		2.89	1b2u → 2eg	95.82	0.062	-0.76	-2.62	-0.13 X 10 ³	-0.46 X 10 ³	
				1a1u → 2eg	2.67						
	1A _{2,u}		2.98	1e1g → 2eg	98.35	0.001	0.00	0.00	-0.73	-0.27 X 10 ³	
	3E _u		3.09	1a2u → 2eg	64.42	0.404	4.30	2.42	1.48 X 10 ³	0.83 X 10 ³	
				2a2u → 2eg	18.18						
				1a1u → 2eg	14.31						
4E _u		3.28	1a2u → 2eg	33.1	2.139	1.48	0.17	-1.52 X 10 ³	-0.17 X 10 ³		
			2a2u → 2eg	30.53							
			1a1u → 2eg	29.57							
NiOEP	1E _u	2.25 ^a	2.31	1a1u → 2eg	57.97	0.034	1.07	5.25	0.04	0.21 X 10 ³	Q
				2a2u → 2eg	40.79						
	2E _u		2.34	2eu → dx ² -y ²	94.42	0.000	0.00	0.44	0.07	0.29 X 10 ³	
				1eu → dx ² -y ²	4.77						
	1A _{2,u}		2.52	39e → 2eg	99.4	0.000	0.00	0.00	0.63	0.44 X 10 ³	
	3E _u		2.56	1b1.u → 2eg	99.34	0.000	-0.00	-2.67	-0.66	-4.30 X 10 ³	
	2A _{2,u}		2.61	1b2u → dx ² -y ²	99.92	0.001	0.00	0.00	0.02	0.06 X 10 ³	
	4E _u	2.88 ^a	3.05	1b2u → 2eg	77.87	0.366	-3.37	-2.07	-2.03 X 10 ³	-1.24 X 10 ³	
1a1u → 2eg				11.15							
2a2u → 2eg				8.89							

ZnOEP	5E _u		3.12	2a2u -> 2eg	42.26	0.920	-1.79	-0.45	2.34 X 10 ³	0.58 X 10 ³	Q
				1a1u -> 2eg	24.14						
				1b2u -> 2eg	19.4						
	6E _u		3.34	1a2u -> 2eg	92.65	0.130	1.27	2.40	-0.47 X 10 ³	-0.89 X 10 ³	
				dxy, dxz -> 1b1u	4.91						
	1E _u	2.21 ^b	2.24	1a1u -> 2eg	53.21	0.019	0.63	5.31	0.02 X 10 ³	0.16 X 10 ³	
				2a2u -> 2eg	45.40						
	2E _u		2.92	1b2u -> 2eg	94.91	0.071	-0.85	-2.58	-0.13 X 10 ³	-0.40 X 10 ³	
	3 E _u		2.96	1a*1u -> 2eg	98.36	0.000	3.96 X 10 ⁻⁴	2.72	-1.69	-0.43 X 10 ³	
	1A _{2,u}		2.98	2a2u -> 1b1u	86.58	0.003	0.00	0.00	-0.60	2.22 X 10 ³	
				1e1u -> 2eg	12.74						
	4E _u	3.16 ^b	3.15	1a2u -> 2eg	54.14	0.620	5.45	2.71	2.86 X 10 ³	1.16 X 10 ⁴	B
				2a2u -> 2eg	24.35						
				1a1u -> 2eg	17.77						
	5E _u		3.27	1a2u -> 2eg	43.51	1.670	3.63	2.033	-2.89 X 10 ³	1.07 X 10 ³	
				2a2u -> 2eg	26.46						
				1a1u -> 2eg	23.58						

^a Ref 70, ^b Ref 78.

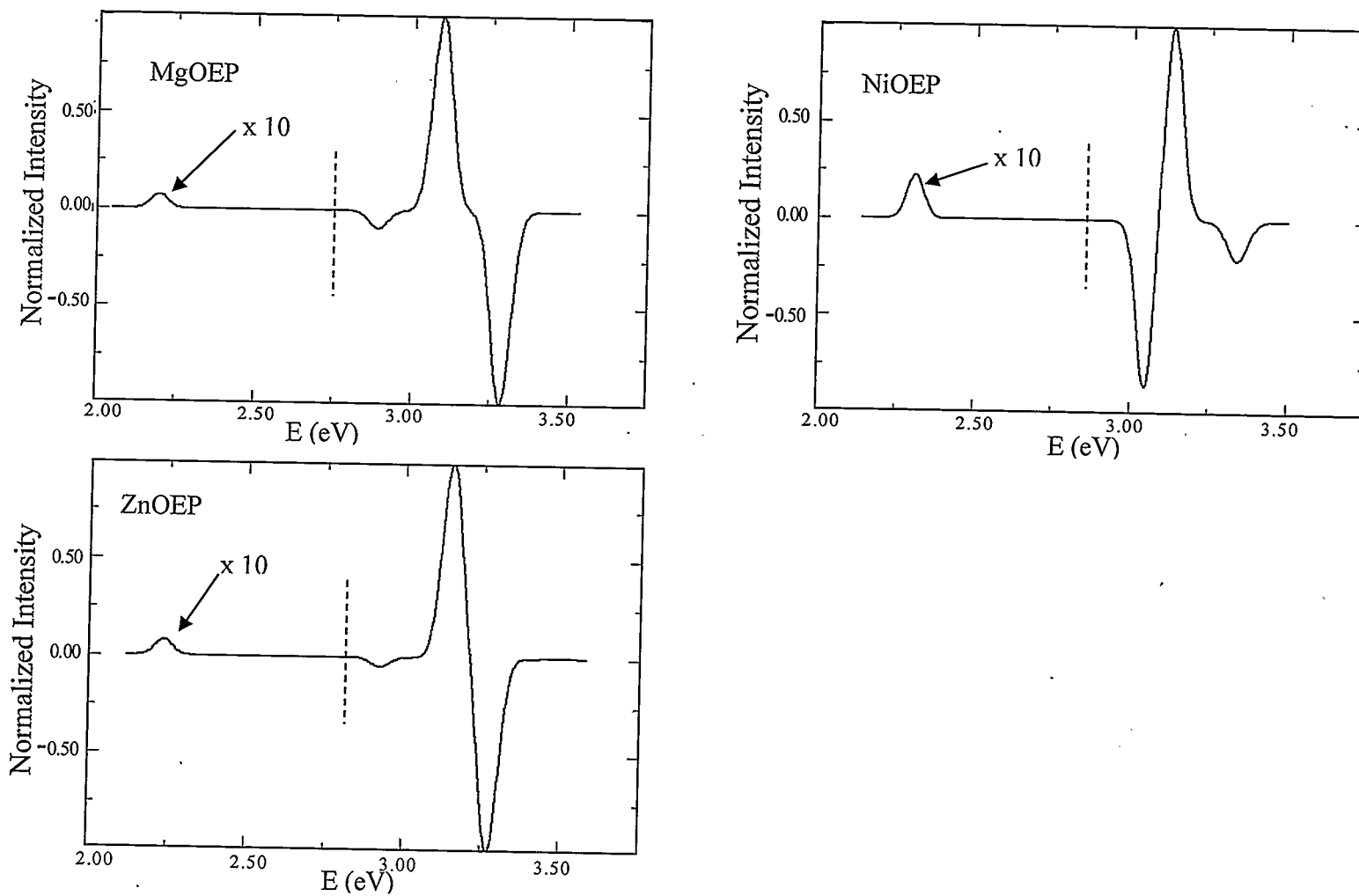


Figure 3.22. Simulated MCD spectrum of MOEP based on B terms alone.

Table 3.6. Some of the relevant integrals used to calculate the A/D term for the Q and B bands of MOEP.

	Zn	Mg	Ni
$\langle e_{1,g}^x \hat{L}_z e_{1,g}^y \rangle^1$	-2.756	-2.765	-2.691
$\langle a_{1,u} \hat{L}_z 2a_{2,u} \rangle^1$	2.577	2.605	2.543

¹Integrals expressed in μB .

For the MgOEP and ZnOEP systems the $1b_{2u} \rightarrow 2e_g$ one-electron transition now appears as $2E_u$ with little or no admixture from the conjugated Gouterman state. The $A_{Ig} \rightarrow 2E_u$ transitions at 2.89 eV and 2.92 eV for MgOEP and ZnOEP, respectively, are both predicted to be very weak, Table 3.5. The two intense transitions are $A_{Ig} \rightarrow 3E_u$ and $A_{Ig} \rightarrow 4E_u$. In MgOEP, $3E_u$ is made up of a $1a_{2u} \rightarrow 2e_g$ transition with some admixture from the conjugated Gouterman state whereas in ZnOEP the dominant one-electron transition is $1a^*_{1u} \rightarrow 2e_g$. Here $1a^*_{1u}$ is an orbital of lower energy but the same symmetry as $1a_{1u}$, see Figure 3.3. For MgOEP the $A_{Ig} \rightarrow 3E_u$ transition takes place at 3.09 eV ($f=4.04$) and is dominated by an intense positive B -term from the magnetic interaction with $4E_u$, Figure 3.23. For ZnOEP the transition $A_{Ig} \rightarrow 3E_u$ is found at 3.15 eV ($f=0.62$). It too is dominated by a large positive B -term from the magnetic interaction with $4E_u$, Figure 3.23 and Table 3.5. Finally, we see that $4E_u$ for both Mg and Zn is represented by the conjugated Gouterman state. It is calculated at 3.28 eV ($f=2.139$) for $M=\text{Mg}$ and 3.27 eV ($f=1.67$) for $M=\text{Zn}$. The $A_{Ig} \rightarrow 4E_u$ transition calculated at 3.27 eV for ZnOEP likely corresponds to the intense band observed for ZnOEP at 3.18 eV [78]. The $4E_u$ states are for $M=\text{Mg}$ as well as Zn dominated by an intense B term from the magnetic coupling with the $3E_u$ state, Figure 3.23. The two B -terms have combined the appearance

of a positive A -term, Figure 3.23. Unfortunately, the experimental [78] MCD spectrum for ZnOEP, has the appearance of a negative A -terms in the Soret region unlike all the other systems we have studied, including NiOEP, Figure 3.20. At the moment we are not in a position to explain why our method in this particular case failed to reproduce experiment. It just should be pointed out that a calculation in which ZnOEP has the structure of Figure 3.18a with D_{4h} symmetry, gave similarly incorrect results for ZnOEP.

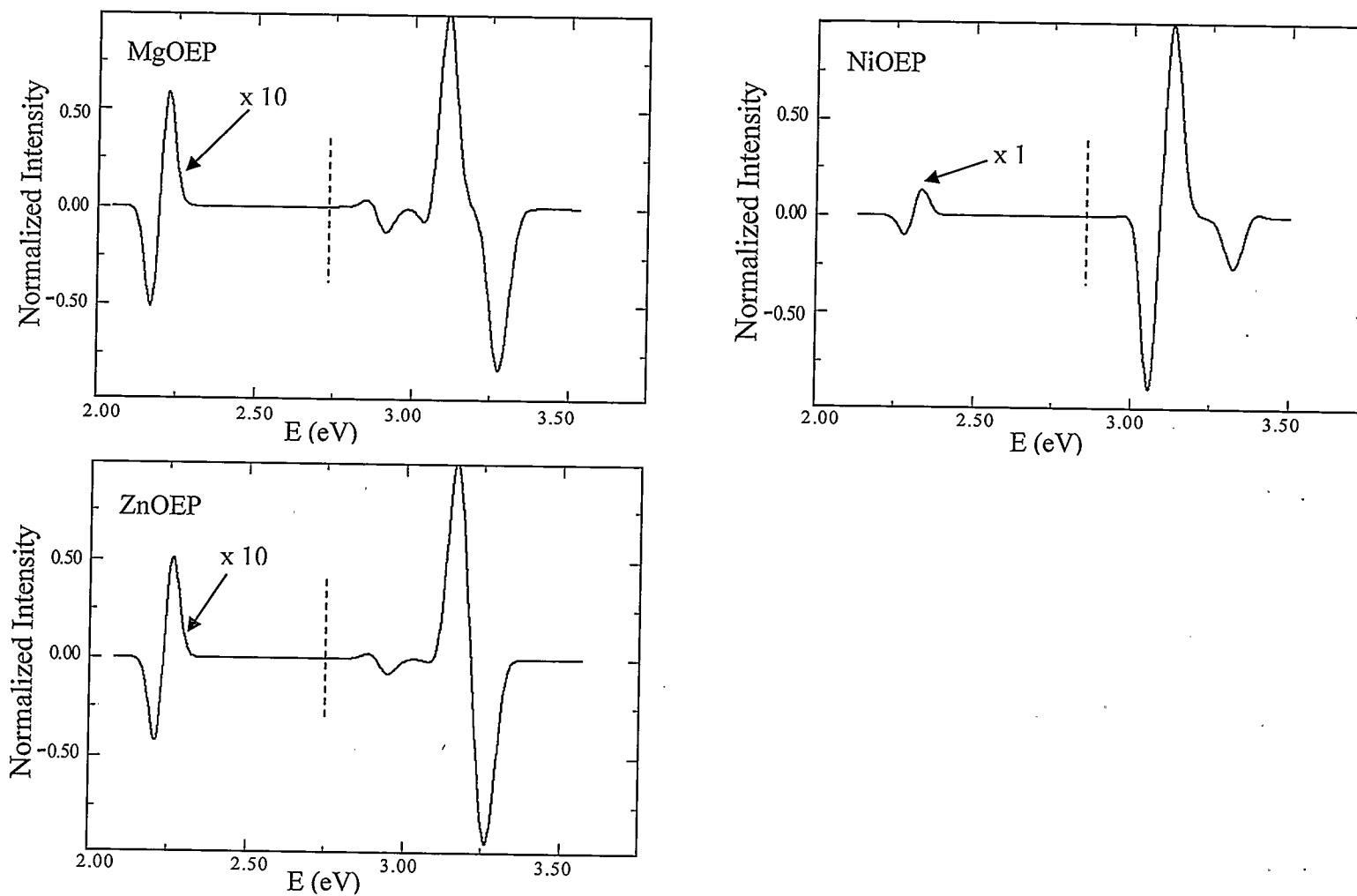


Figure 3.23. Simulated MCD spectrum of MOEP based on A and B terms combined

4. RESULTS AND DISCUSSION FOR MODIFIED METAL PORPHYRINS (MTAP, MPC)

4.1 Detailed Discussion of Simulated MCD Spectra for MTAP

Having analyzed the basic porphyrins and the effect of substituting phenyl groups in the m positions and ethyl groups in the β positions, a new modification of the porphyrin ring was explored: the aza substitution. We shall start with the simplest of the next group of porphyrin derivatives, the tetraazaporphyrin (MTAP, $M=\text{Zn, Mg, Ni}$), which consists in an aza substitution in the m positions of the porphyrin ring.

The $2a_{2u}$ orbital of the regular porphyrins (MP, MTPP and MOEP) has a large contribution from the π orbital of the carbon atom in the m -position. As the carbon atom now is substituted by the more electronegative nitrogen in MTAP, the energy of $2a_{2u}$ is lowered compared to $1a_{1u}$ where the composition is unchanged. We present the key orbitals in the aza-porphyrins in Figure 4.1 exemplified by NiTAP orbitals. The corresponding orbitals of regular porphyrins are given in Figure 3.7.

The lowering of the $2a_{2u}$ orbital in aza-porphyrins lifts the degeneracy between $2a_{2u}$ and $1a_{1u}$ observed in regular porphyrins. Thus, we now have in MTAP a Q -band that has 85-75 % contribution from the $1a_{1u} \rightarrow 2e_g$ one-electron transition and 15-25 % contribution from the $2a_{2u} \rightarrow 2e_g$ one electron transition. In the regular porphyrins with a 50/50 contribution from the two one electron transitions the calculated intensity of the Q -band is low as the two transitions contribute with opposite signs to the oscillatory strength f . In TAP such a cancellation is not possible and we find an intense Q -band with

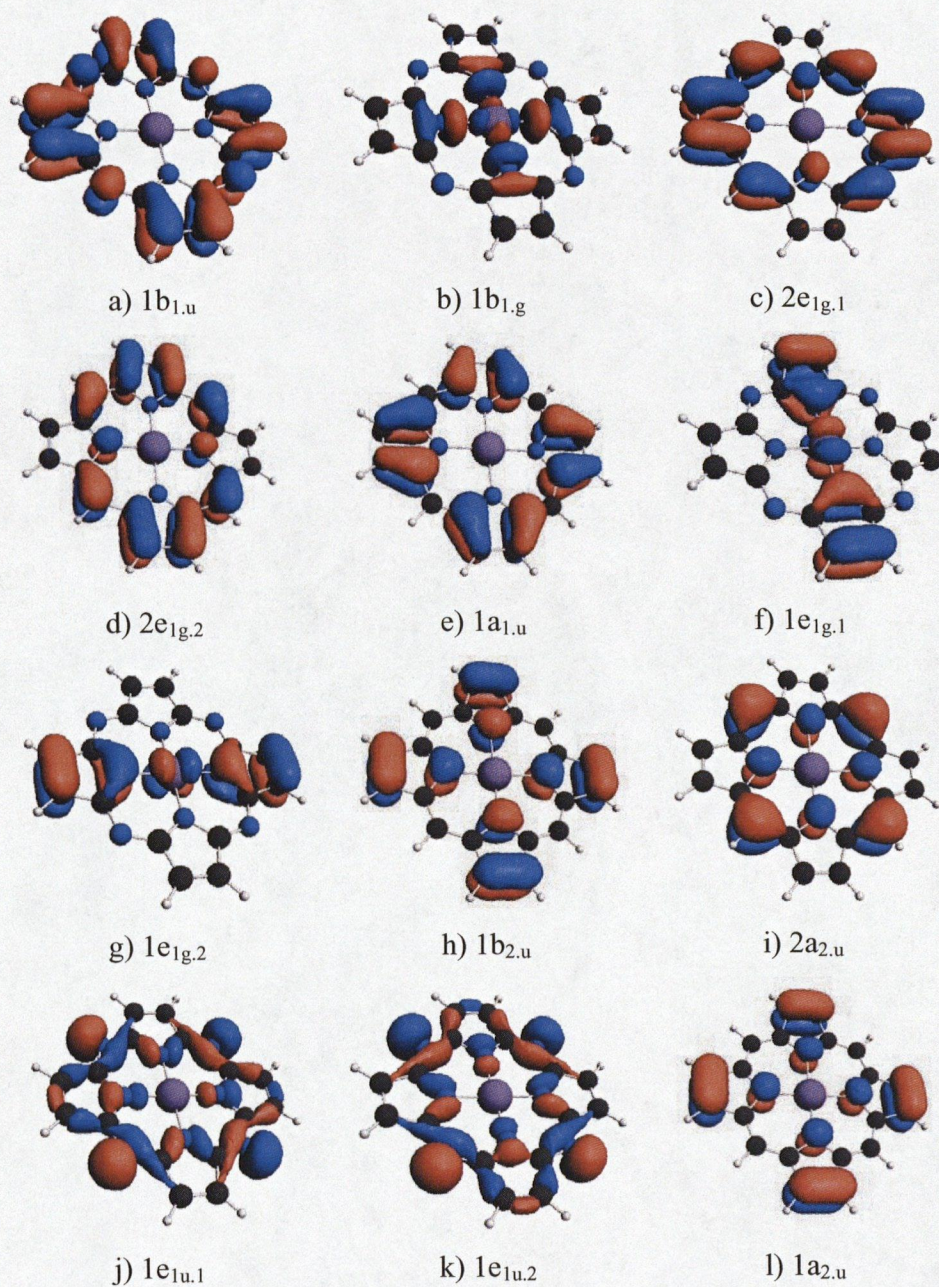


Figure 4.1 Most relevant orbitals for tetraazaporphyrin systems. The orbitals $1e_{1g}$ and $1b_{1g}$ are depicted for the NiTAP as they differ from the similar ones for MgTAP and ZnTAP where they do not play an active role.

$f = 0.25 - 0.5$. The experimental MCD spectrum for ZnTAP clearly reveals a positive A term in the Q-band region, Figure 4.2, in agreement with our findings, Table 4.1 and Figure 4.3.

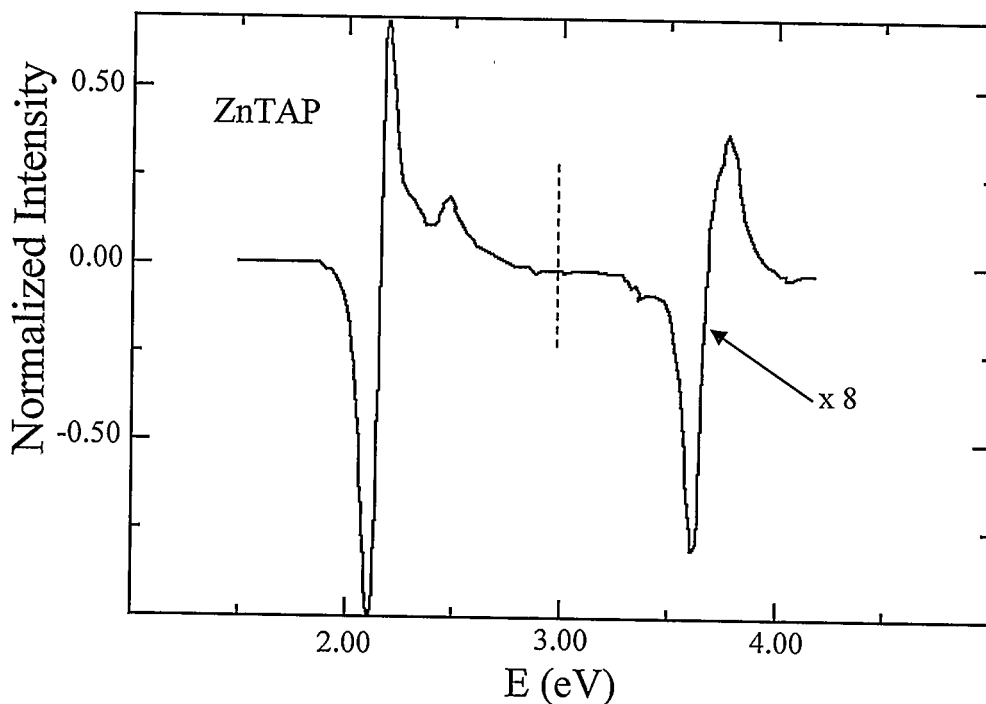


Figure 4.2. Experimental MCD spectrum for ZnTAP [80].

The positive A/D term is understandable if we make use of the same analysis as in Chapter 3 based on the equations 3.1 and 3.3. For MTAP we have $c_1 \approx 1$ whereas $c_2 \approx 0$, $c_3 = 0.0$, $c_4 = 0.0$. Thus, the first term in Equation 3.8 $T_1 = -(c_1^2 + c_2^2 - c_3^2 + c_4^2) \langle e_g^x | \hat{L}_z | e_g^y \rangle$ will contribute with a positive value as in previous ligands since the sign of $\langle e_g^x | \hat{L}_z | e_g^y \rangle$ is negative, see Tables 4.1 and 4.2. The calculated A-terms for the Q band of the three MTAP systems are very similar with values of 6.86

Table 4.1. Calculated excitation energies (eV), oscillator strength (f) and A, A/D, B and B/D terms for MTAP (M=Mg, Ni, Zn).

Complex	Symmetry	Excitation energies		Composition	%	f	A ($D^2\mu_B$)	A/D (μ_B)	B	B/D	Assign.
		exp.	calc.								
MgTAP	1E _u	2.32	1a1.u -> 2e.g 2a2.u -> 2e.g	74.82 20.89	0.474	6.86	4.94	0.17 X 10 ⁻³	0.12 X 10 ⁻³	Q	
	2E _u	2.79	1b2.u -> 2e.g	97.27	0.048	-0.31	-2.64	0.04 X 10 ⁻³	0.37 X 10 ⁻³		
	1A _{2,u}	3.04	1e.u -> 2e.g	99.02	0.001	0.00	0.00	3.73	0.66 X 10 ⁻³		
	3E _u	3.08	1a2.u -> 2e.g 2a2.u -> 2e.g	61.32 34.07	0.088	0.55	2.87	0.09 X 10 ⁻³	0.46 X 10 ⁻³	B ₁	
	4E _u	3.70	2a2.u -> 2e.g 1a2.u -> 2e.g 1a1.u -> 2e.g	42.25 31.79 1.84	3.280	1.33	0.22	-0.34 X 10 ⁻³	-0.06 X 10 ⁻³	B ₂	
	NiTAP	1E _u	2.39	1a1.u -> 2e.g 2a2.u -> 2e.g	83.58 13.78	0.522	6.76	4.56	0.19 X 10 ⁻³	0.13 X 10 ⁻³	Q
	2E _u	2.98	1b2.u -> 2e.g	97.11	0.046	-0.27	-2.59	0.02 X 10 ⁻³	0.19 X 10 ⁻³		
	1A _{2,u}	3.29	1e.u -> 2e.g	98.76	0.001	0.00	0.00	3.32	0.81 X 10 ⁻³		
	3E _u	3.34	1a2.u -> 2e.g 1e.g -> 1b1.u	84.67 12.74	0.004	0.02	2.27	-3.87	-0.54 X 10 ⁻³		
	2A _{2,u}	3.44	1b2.u -> 1b1.g	99.84	0.000	0.00	0.00	-0.12	-0.13 X 10 ⁻³		
	4E _u	3.47	1e.g -> 1b1.u 2a2.u -> 2e.g	52.35 35.58	0.230	0.12	0.27	-0.23 X 10 ⁻³	-0.50 X 10 ⁻³	B ₁	
	5E _u	3.69	1e.u -> 1b1.g	42.18	0.574	-0.58	-0.55	-0.18 X 10 ⁻³	-0.17 X 10 ⁻³	B ₂	

				1e.g	->	1b1.u	25.55						
				2a2.u	->	2e.g	17.54						
				1a2.u	->	2e.g	8.65						
ZnTAP	1E _u	2.13 ^a	2.35	1a1.u	->	2e.g	77.68	0.258	7.29	4.89	0.20 X 10 ⁻³	0.13 X 10 ⁻³	Q
				2a2.u	->	2e.g	18.75						
	2E _u		2.83	1b2.u	->	2e.g	97.33	0.024	-0.30	-2.64	0.04 X 10 ⁻³	0.35 X 10 ⁻³	
	1A _{2,u}		3.10	1e.u	->	2e.g	98.93	0.001	0.00	0.00	3.40	0.75 X 10 ⁻³	
	3E _u	3.44 ^a	3.16	1a2.u	->	2e.g	73.81	0.015	0.18	2.83	0.04 X 10 ⁻³	0.67 X 10 ⁻³	B ₁
				2a2.u	->	2e.g	23.09						
	4E _u	3.73 ^a	3.69	2a2.u	->	2e.g	54.59						
				1a2.u	->	2e.g	20.14	1.446	1.55	0.29	-0.31 X 10 ⁻³	-0.06 X 10 ⁻³	B ₂
				1a1.u	->	2e.g	17.05						

^a Ref 80.Table 4.2. Some of the relevant integrals used to calculate the A/D term for the *Q* and *B* bands of MTAP.

	Zn	Mg	Ni
$\langle e_{1,g}^x \hat{L}_z e_{1,g}^y \rangle^1$	-2.7287	-2.7486	-2.6325
$\langle a_{1,u} \vec{L}_z 2a_{2,u} \rangle^1$	1.1216	1.1481	0.6809

¹Integrals expressed in μB .

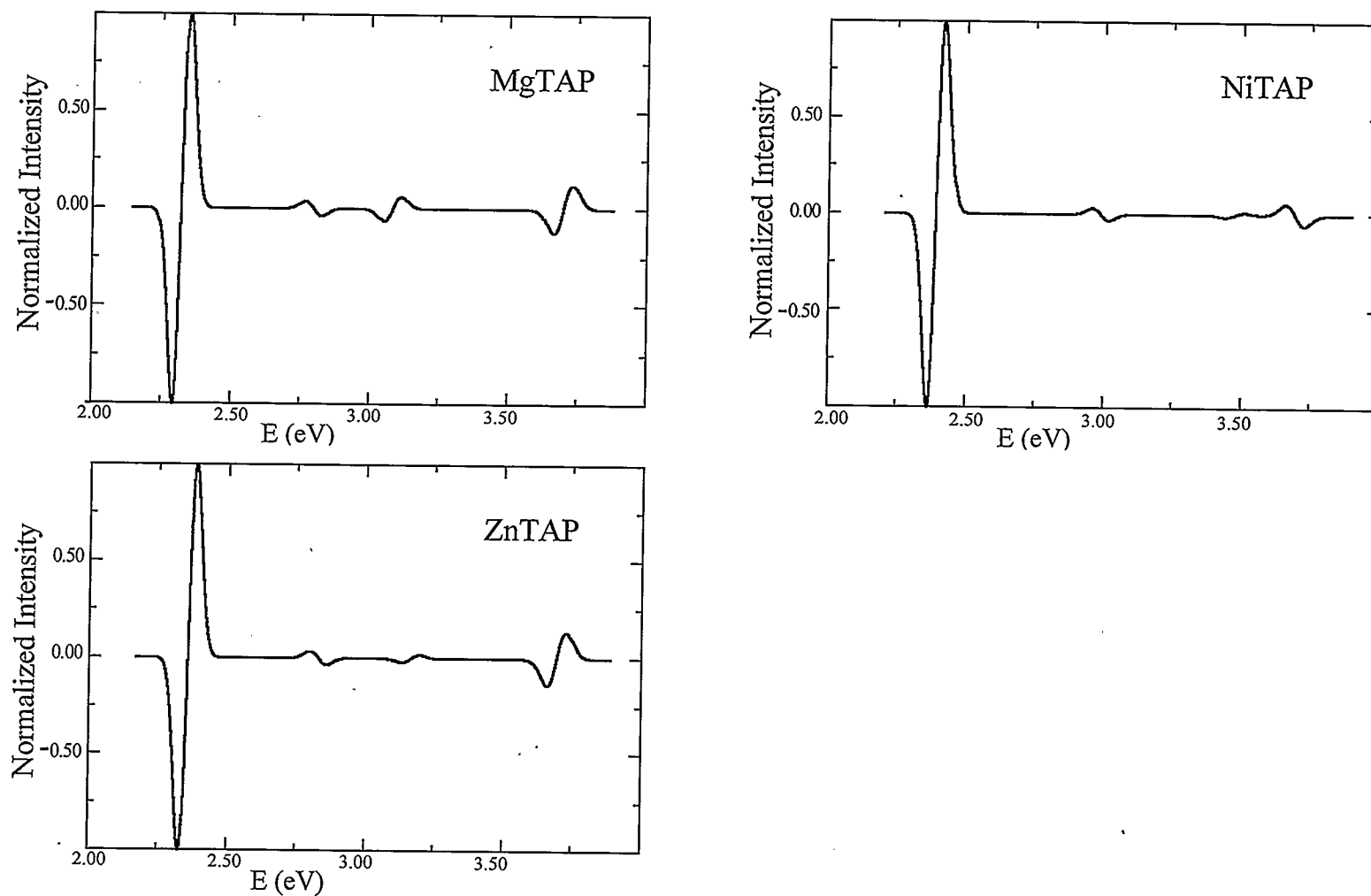


Figure 4.3. Simulated MCD spectra of MTAP based on A terms alone where $M=\{\text{Mg, Ni, Zn}\}$.

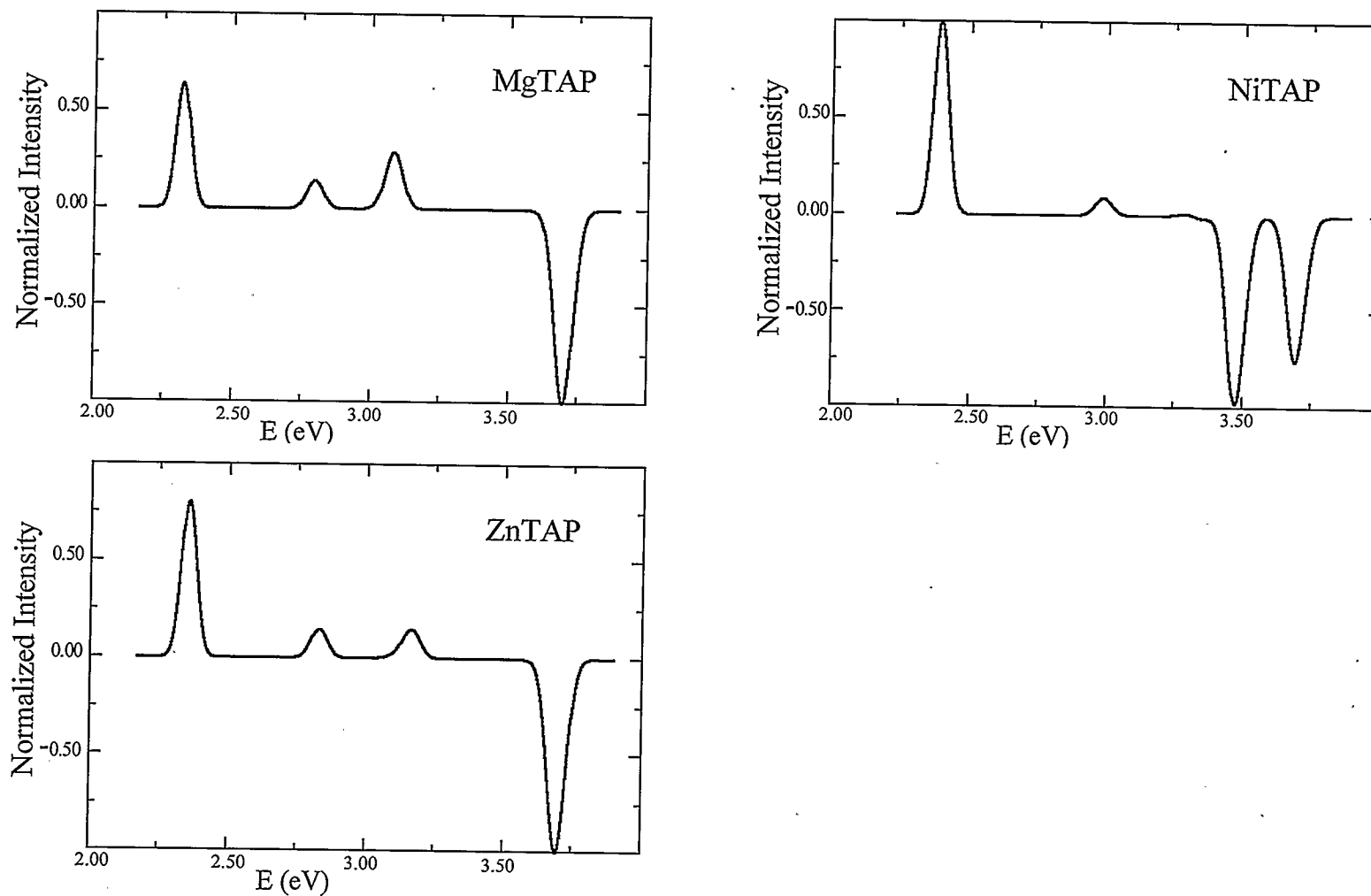


Figure 4.4 Simulated MCD including only the B terms due to the mixing of different excited states for the MTAP systems.

$D^2\mu_B$, $6.76 D^2\mu_B$ and $7.29 D^2\mu_B$ at the calculated excitation energies of 2.32, 2.39, and 2.35 eV for Mg, Ni and Zn TAP, respectively. These values are much larger than for the regular porphyrins and reflect the larger intensity gained from lifting the near degeneracy between the $1a_{1u} \rightarrow 2e_g$ and $2a_{2u} \rightarrow 2e_g$ transitions. However, it is interesting that the corresponding calculated A/D values of $4.94 \mu_B$, $4.56 \mu_B$, and $4.89\mu_B$, Table 4.1, are similar to those found for the regular porphyrins. The three MTAP complexes exhibit in addition a medium size positive B term, Table 4.1 and Figure 4.4 in the Q -band region due to the $A_{1g} \rightarrow 1E_u$ transition. The B makes the A -term in the combined simulated MCD spectrum appear unsymmetrical with the positive lobe larger than the negative lobe, Figure 4.5. The experimental MCD spectrum of ZnTAP seems to reveal that the negative lobe is largest.

For the regular porphyrins the Soret region is dominated by two excitations due to the $1b_{2u} \rightarrow 2e_g$ one electron transition and the conjugated Gouterman band ($1a_{1u} \rightarrow 2e_g$ and $2a_{2u} \rightarrow 2e_g$), respectively. Further, the excitation represented by $1b_{2u} \rightarrow 2e_g$ gains some intensity by mixing with the Gouterman band. The simulated MCD spectrum is dominated by a pseudo-A term made up of two B-terms of opposite sign from each of the transitions.

The Soret region for the aza systems MgTAP and ZnTAP which we shall discuss next is dominated by the three one electron excitations $1b_{2u} \rightarrow 2e_g$, $2a_{2u} \rightarrow 2e_g$ and $1a_{2u} \rightarrow 2e_g$, Table 4.1. The $1b_{2u} \rightarrow 2e_g$ transition gives rise to the $A_{1g} \rightarrow 2E_u$ excitation with calculated absorption energy of 2.8 eV. The transition has a small negative A term, Table 4.1 and Figure 4.3, and a positive B-term, Figure 4.4. In the complete MCD simulation where A and B terms are combined, $2E_u$ exhibits a positive B-term at 2.8 eV

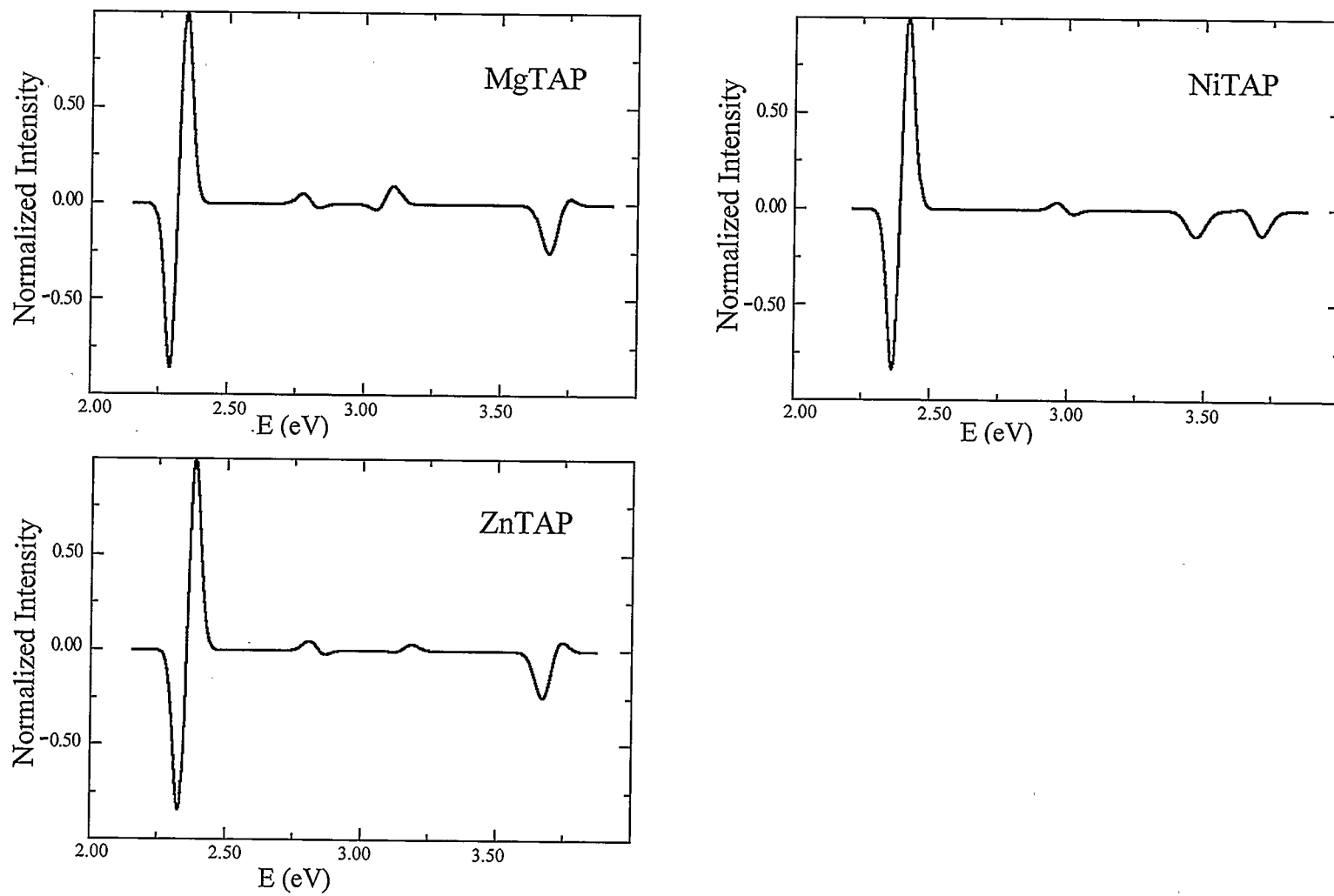


Figure 4.5. Simulated MCD spectra including both A and B terms for the MTAP systems.

for both MgTAP and ZnTAP, Figure 4.5. It might well correspond to the feature in the experimental MCD spectrum for ZnTAPP observed at 2.5 eV at the onset of the Soret region right after the large A term due to E_u , Figure 4.6.

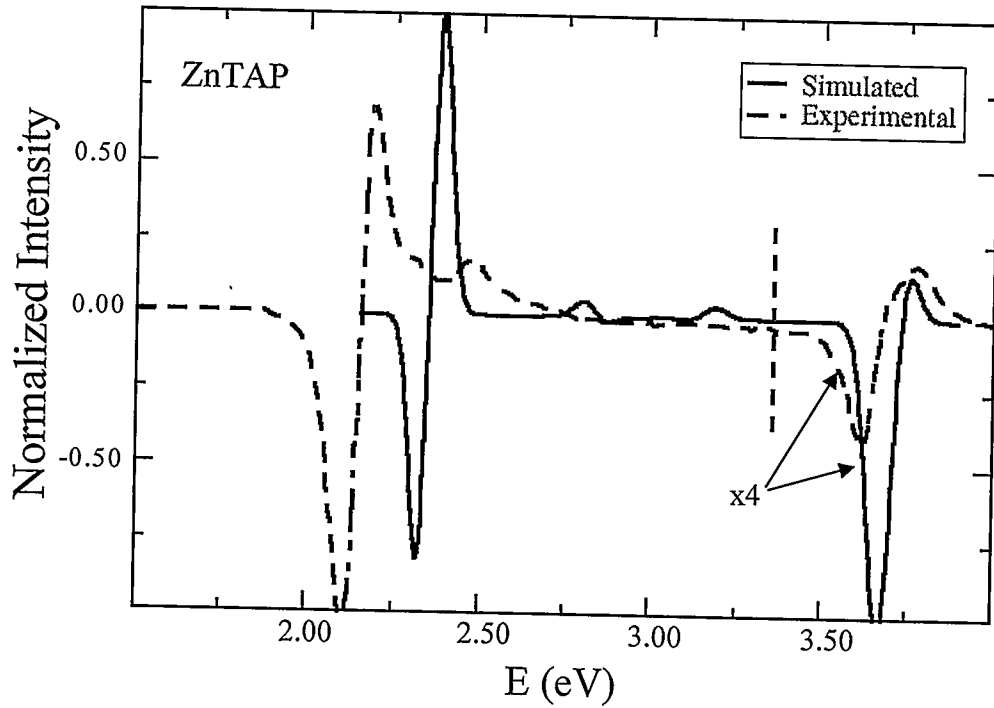


Fig. 4.6 Simulated and experimental [80] MCD of ZnTAP including both A and B terms in the simulation.

The $2a_{2u} \rightarrow 2e_g$ and $1a_{2u} \rightarrow 2e_g$ transitions couple into the $A_{1g} \rightarrow 3E_u$ and $A_{1g} \rightarrow 4E_u$ excitations of which the first calculated at 3.08 to 3.16 eV is weak ($f = 0.1$ to $f = 0.16$), whereas the second at 3.7 eV is strong ($f = 3.28$ to $f = 1.15$), Table 4.1. The excited state $3E_u$ exhibits for $M = \text{Mg, Zn}$ positive A and B terms with $A/D = 2.87 - 2.80 \mu_B$, Table 4.1 and Figures 4.2 and 4.4. In the simulated MCD spectrum, Figure 4.6, $3E_u$ exhibits a positive B -term at 3.1 to 3.2. eV. It does not seem to find its match in the

experimental MCD spectrum of ZnTAP, Figure 4.6, [80]. The $4E_u$ state is represented by a relatively strong positive A -term ($1.33 - 1.55 D^2 \mu_B$), Figure 4.2, and a negative B -term, Figure 4.4. In the combined MCD simulation $4E_u$ appears with a positive A -term made asymmetric by a negative B -term, Figure 4.5, in good agreement with experiment for ZnTAP, Figure 4.6. It is also in agreement with the experiment that the simulated MCD spectrum in the Q -region with one positive A -term is more intense than the positive A -term in the Soret region, Figure 4.6.

The calculated spectrum for NiTAP in the Soret region is more complicated than for MgTAP and ZnTAP due to the additional participation of the $1e_u \rightarrow 1b_{1g}$ and the $1e_g \rightarrow 1b_{1u}$ one electron transitions. The new orbitals introduced are shown in Figure 4.1. In the simulated MCD spectrum of NiTAP we note for the Soret region that $2E_u$ ($1b_{2u} \rightarrow 2e_{1g}$) appear as a weak negative A -term as for MgTAP and ZnTAP, Figure 4.5. We have in addition for the $A_{1g} \rightarrow 4E_u$ ($1e_g \rightarrow 1b_{1u}$; $2a_{2u} \rightarrow 2e_g$) and $A_{1g} \rightarrow 5E_u$ ($1e_u \rightarrow 1b_{1g}$; $1e_g \rightarrow 1b_{1u}$) excitation with medium strong B -terms, Table 4.1 and Figures 4.4 and 4.5. Unfortunately, to date no experimental MCD spectrum has been published for comparison.

4.2 The MCD Spectra of the Phthalocyanine Complexes MgPc and ZnPc

The phthalocyanine ligand (Pc) differs from the simple porphyrin (P), see Figure 2.1, in having substantial substitutions in both the m and the β positions, see Figure 3.7. We have already seen from the porphyrazine complexes MTAP that an aza substitution in the m positions gives rise to a lowering in energy of the $2a_{2u}$ orbital, Figure 4.7. This

MP

MTAP

MPc

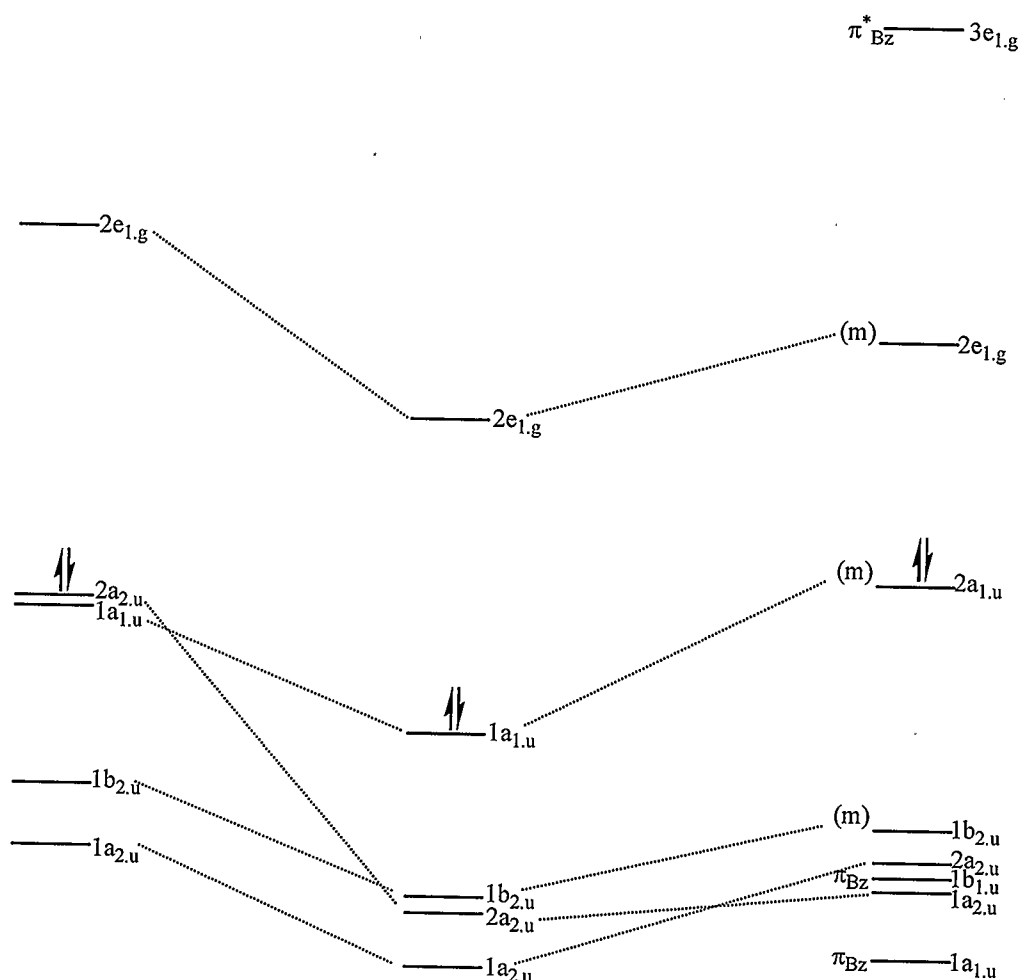


Figure 4.7. Comparison of the most relevant molecular orbitals for MP, MTAP and MPc. The actual distribution was made using ZnL (L=P, TAP, Pc) molecular orbitals as a reference.

orbital is, in the MP systems, degenerate with the $1a_{1u}$ orbital, Figure 4.7. The result of the $2a_{2u}$ stabilization is that the Q-band in the MTAP systems of Section 4.1 mostly was made up of the $1a_{1u} \rightarrow 2eg$ transition, Table 4.1, whereas it is a 50:50 mixture of $1a_{1u} \rightarrow 2eg$ and $2a_{2u} \rightarrow 2eg$ for MP. On the other hand, the Soret band which in MP is

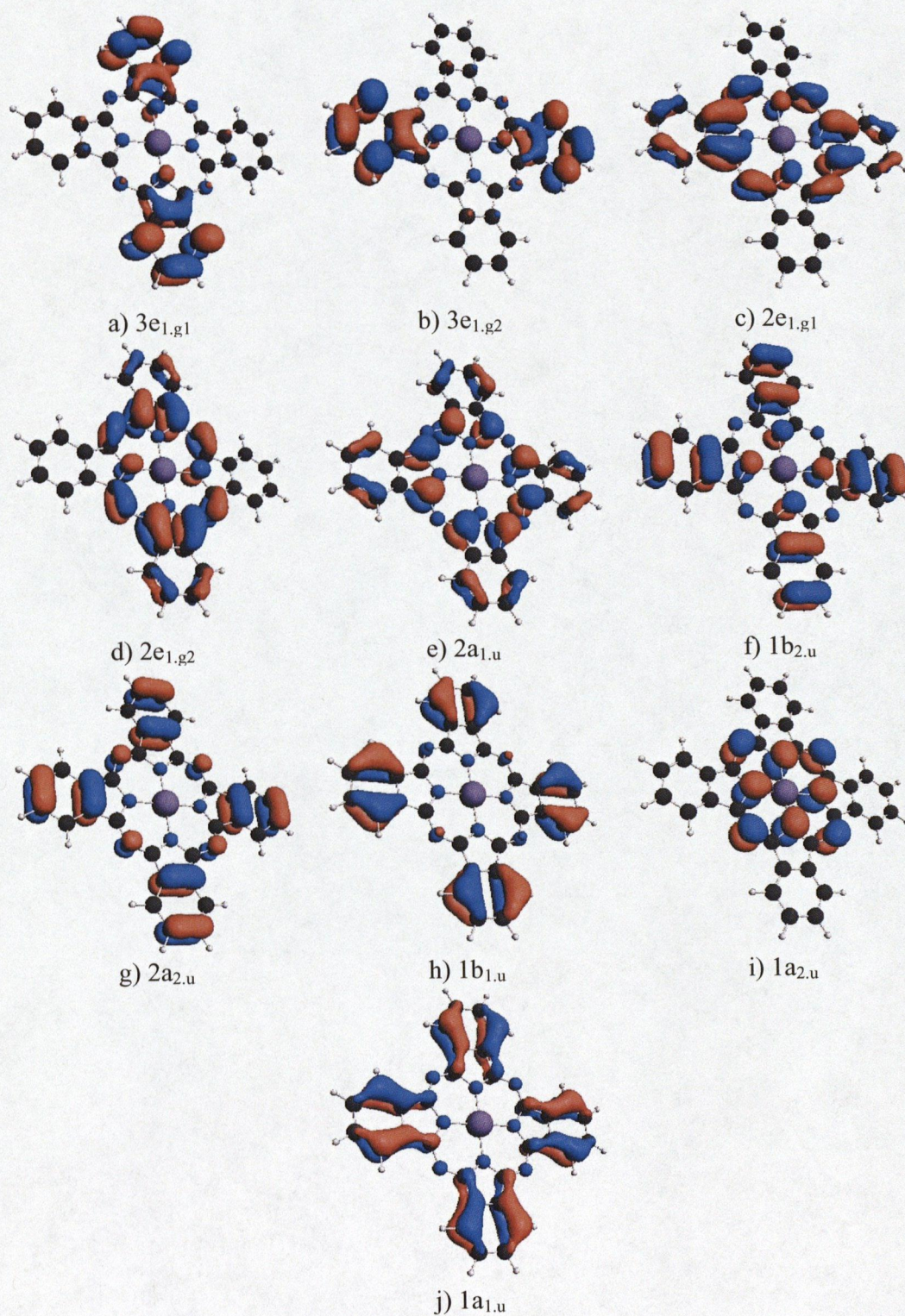


Figure 4.8. Most relevant orbitals of phthalocyanine systems.

dominated by two excitations, namely the conjugated Gouterman band ($50:50\ 1a_{1u} \rightarrow 2e_g$ and $2a_{2u} \rightarrow 2e_g$) and the $1b_{2u} \rightarrow 2e_g$ transition, is in the MTAP systems ($M=\text{Mg,Zn}$) made up of the $1b_{2u} \rightarrow 2e_g$ one electron transition and a mixture of $2a_{2u} \rightarrow 2e_g$ and $1a_{1u} \rightarrow 2e_g$.

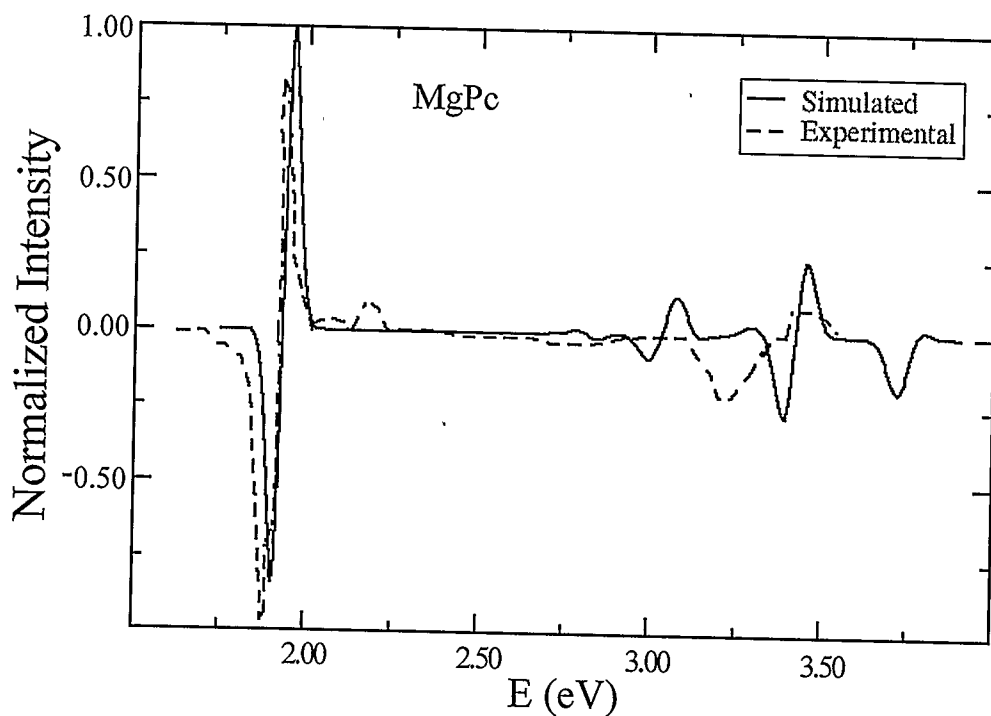


Figure 4.9. Experimental and Simulated MCD spectra for MgPc [84].

Apart from the aza substitution in the m position, MPc also has the addition of a butadiene unit to the 4 pairs of adjacent β carbons to form 4 fused benzene rings, see Figure 2.1e. The fused rings give rise to 3 new orbitals representing the upper occupied and lower unoccupied valence levels, Figure 4.7. Of these orbitals $3e_g$ is empty and made up of π_{Bz}^* on the different rings, Figure 4.8, whereas the occupied levels $1b_{1u}$ and $1a_{1u}$ are

are represented by the benzene HOMO orbitals π_{Bz} , Figures 4.7 and 4.8. In addition $2e_{1g}$ and $2a_{1u}$ are constructed from $2e_{1g}$ and $1a_{1u}$ of MTAP by adding an out-of-phase contribution from the butadiene HOMO orbital π_2 . Finally we have that $1b_{2u}$ and $2a_{2u}$ are constructed from $1b_{2u}$ and $1a_{2u}$ of MTAP by adding π_1 and π_3^* from butadiene, Figures 4.7 and 4.8. One can also consider $1b_{2u}$ and $2a_{2u}$ as linear combinations of π_{Bz} ring orbitals, Figure 4.8.

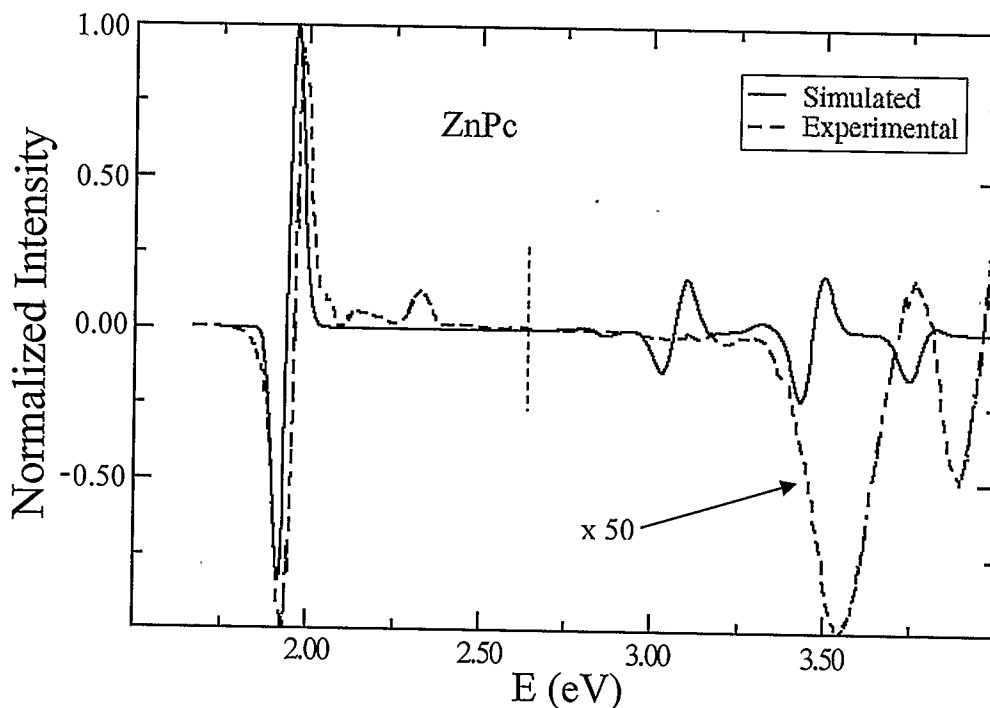


Figure 4.10 Experimental MCD spectrum corresponds to $\text{ZnPc}(-2)\text{Im}_2$ [82].

We shall now turn to an assignment of the experimental MCD spectra for MgPc , Figure 4.9, and ZnPc , Figure 4.10, based on our simulated spectra, Figure 4.11 as well as Figures 4.12 and 4.13. Our simulations included both A -terms, Figure 4.11, and B -terms

4E _{1,u}	3.11	1b1.u -> 2e.g	76.01	0.310	-2.09	-1.54	0.97 X 10 ³	0.71 X 10 ³	B ₁
		2a2.u -> 2e.g	10.43						
		2a1.u -> 3e.g	5.77						
		1a2.u -> 2e.g	4.38						
5E _{1,u}	3.32	2a1.u -> 3e.g	88.42	0.036	-0.11	-0.76	0.16 X 10 ³	1.09 X 10 ³	
		1b1.u -> 2e.g	5.13						
1A _{2,u}	3.34	1e.u -> 2e.g	99.14	0.001	0.00	0.00	0.01 X 10 ³	3.89 X 10 ³	
6E _{1,u}	3.46	1a1.u -> 2e.g	46.39	0.640	7.92	3.15	-0.21 X 10 ³	-0.08 X 10 ³	
		1a2.u -> 2e.g	39.99						
		2a2.u -> 2e.g	7.51						
7E _{1,u}	3.74 ^b 3.76	1a1.u -> 2e.g	46.97	1.069	3.00	0.78	-0.72	-0.19 X 10 ³	B ₂
		1a2.u -> 2e.g	31.18						
		2a2.u -> 2e.g	7.19						

^a Ref 82, ^b Ref 83.

Figure 4.12. The Q-band is exclusively made up of a $2a_{1u} \rightarrow 2e_g$ one electron transition and the excitation energies for $A_{1g} \rightarrow 1E_u$ of 1.93 eV (Mg) and 1.94 eV (Zn) are in good agreement with the experimental values of 1.85 eV (Mg) and 1.88 eV (Zn), Table 4.3. We compare in Figure 4.14 the simulated and experimental absorption spectra. The simulated MCD spectra in the Q-band region contain an intense positive A -term, Figure 4.12, and a weak B -term, Figure 4.13, that combined appear as a positive A -term, Figures 4.11, in agreement with experiments, Figures 4.9 and 4.10. The calculated A/D values of 4.04 for MgPc and 3.98 for ZnPc, Table 4.3, are in reasonable agreement with the experimental values of 2.68 for MgPc [82] and 4.2 for ZnPc [83].

Our calculations predict the existence of a number of transitions of low intensity in the region between 2.80 eV and 3.35 eV, Figure 4.14 and Table 4.3. Of these $1A_{1g} \rightarrow 2E_u$ ($1b_{2u} \rightarrow 2e_g$) and $A_{1g} \rightarrow 3E_u$ ($2a_{2u} \rightarrow 2e_g$) are similar in energy and composition to the corresponding transitions in MTAP. Others, such as $A_{1g} \rightarrow 4E_u$ ($1b_{1u} \rightarrow 2e_g$) and $A_{1g} \rightarrow 5E_u$ ($2a_{2u} \rightarrow 3e_g$) involve either a transition from a π_{Bz} -ring combination ($1b_{1u}$) or the transition to a π_{Bz}^* -ring combination ($3e_{g1}$). The transitions $A_{1g} \rightarrow nE_u$ ($n=2,5$) are weak and situated at the onset of the broad band observed with a maximum around 3.5 eV, Figure 4.14. It is thus not likely that they can be observed (distinguished) individually.

We find for both MgPc and ZnPc that the Soret band is made up of the two transitions both constructed from the $1a_{1u} \rightarrow 2e_g$ and $1a_{2u} \rightarrow 2e_g$ one electron transitions. The first transition $A_{1g} \rightarrow 6E_u$ is calculated at 3.42 eV (Mg) and 3.46 eV (Zn), respectively, whereas the second ($A_{1g} \rightarrow 7E_u$) is predicted at 3.65 eV for MgPc and 3.70

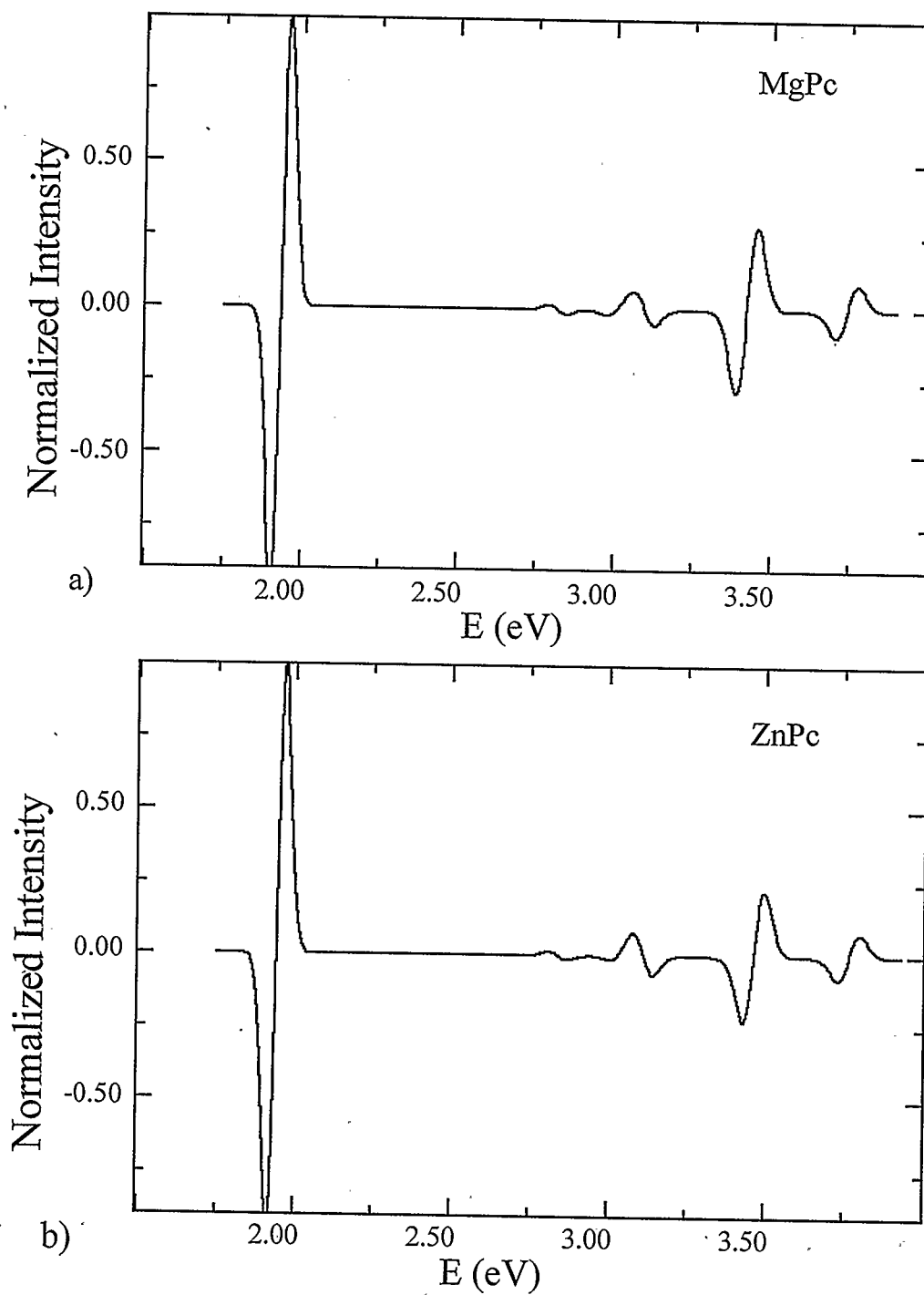


Figure 4.11. Simulated MCD spectra of MPc based on A -terms alone where $M =$ a) Mg, b) Zn..

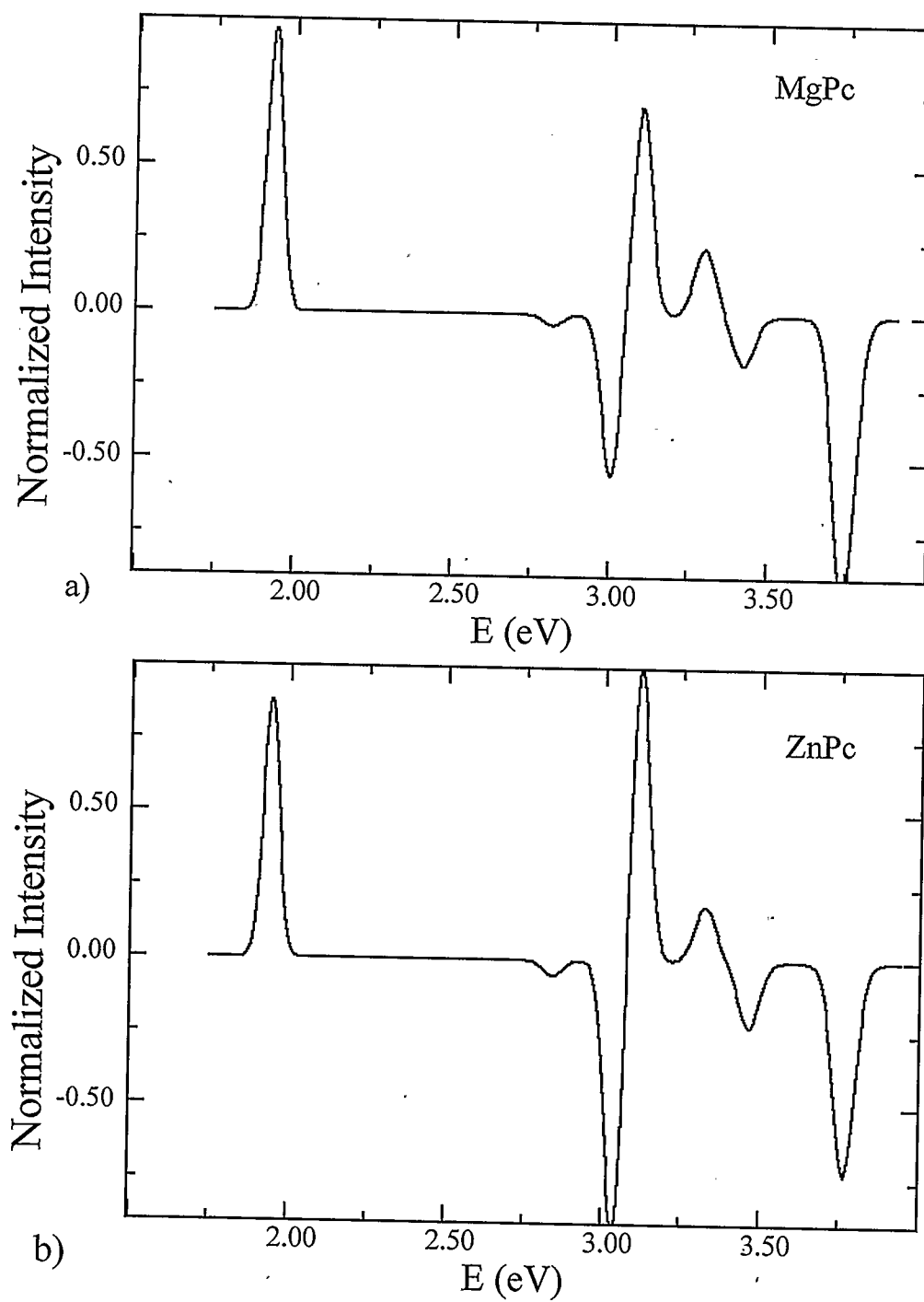


Figure 4.12. Simulated MCD spectra of MPc based on B terms alone where M = a) Mg, b) Zn.

eV for ZnPc, Table 4.3 and Figure 4.14. We note further that both the $A_{Ig} \rightarrow 6E_u$ and the $A_{Ig} \rightarrow 7E_u$ transitions have a large oscillator strength with an intensity ratio of 6:10. We assign both of these transitions to the broad Soret band observed around 3.5 eV for the two compounds. The $A_{Ig} \rightarrow 6E_u$ transition has a large positive A -term and a small negative B -term, Table 4.3 and Figure 4.12-4.13, which combined look like a positive A -term, Figure 14.3. On the other hand, the $A_{Ig} \rightarrow 7E_u$ transition has a negative B -term and a smaller positive A -term which combined appear as a negative B -term. Table 4.3 and Figures 4.12-4.13. Our simulated MCD spectrum in the Soret region is quite similar for MgPc and ZnPc, in agreement with experiment. The recorded MCD spectrum in the Soret region appears as one broad and positive A -term which we assign to the $A_{Ig} \rightarrow 6E_u$ transition. It should be pointed out that the experimental MCD spectrum presented in Figure 4.10 is multiplied by ~ 50 whereas the simulated spectrum is unscaled.

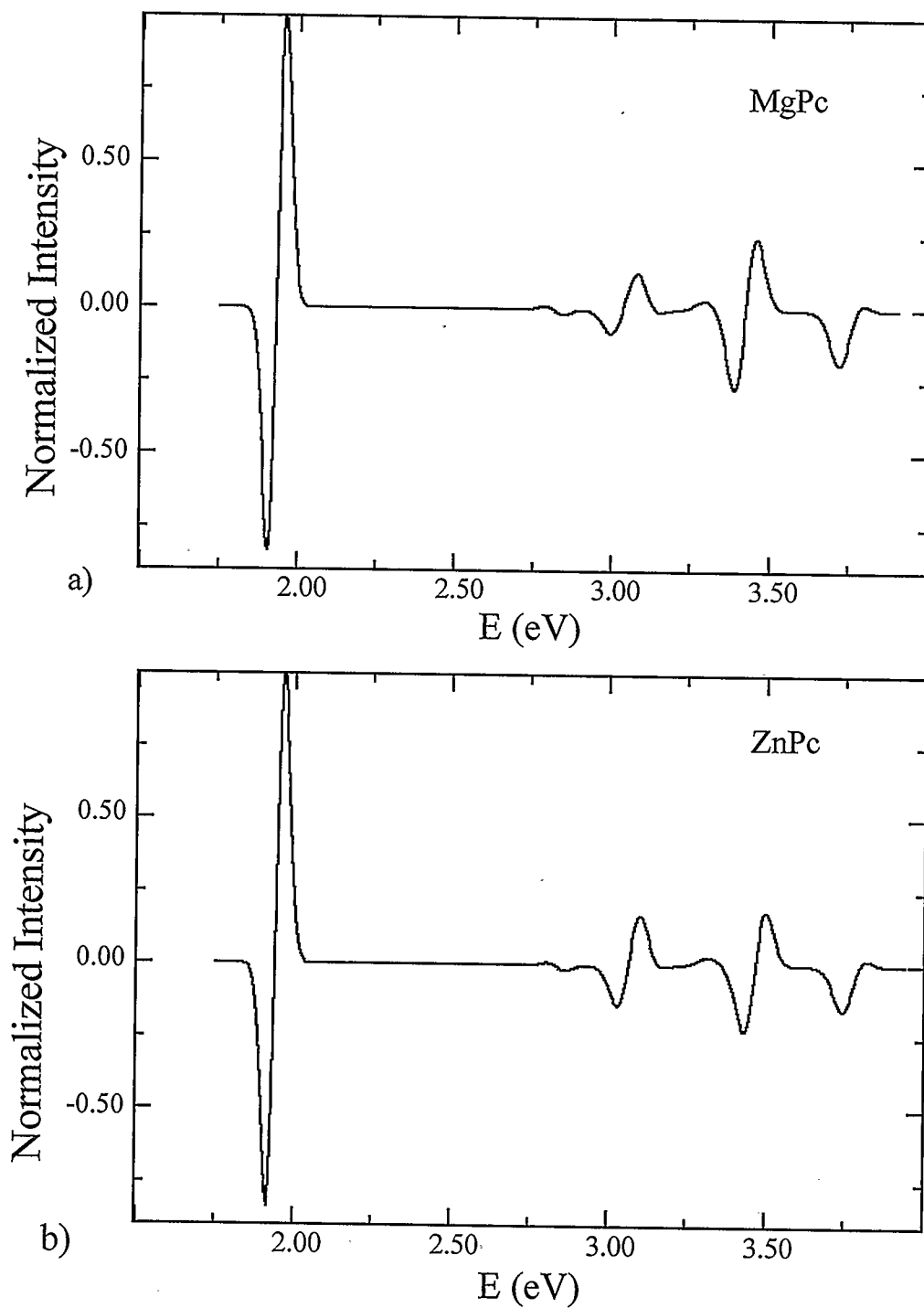


Figure 4.13. Simulated MCD spectra of MPc based on both A and B terms where M = a)Mg, b) Zn.

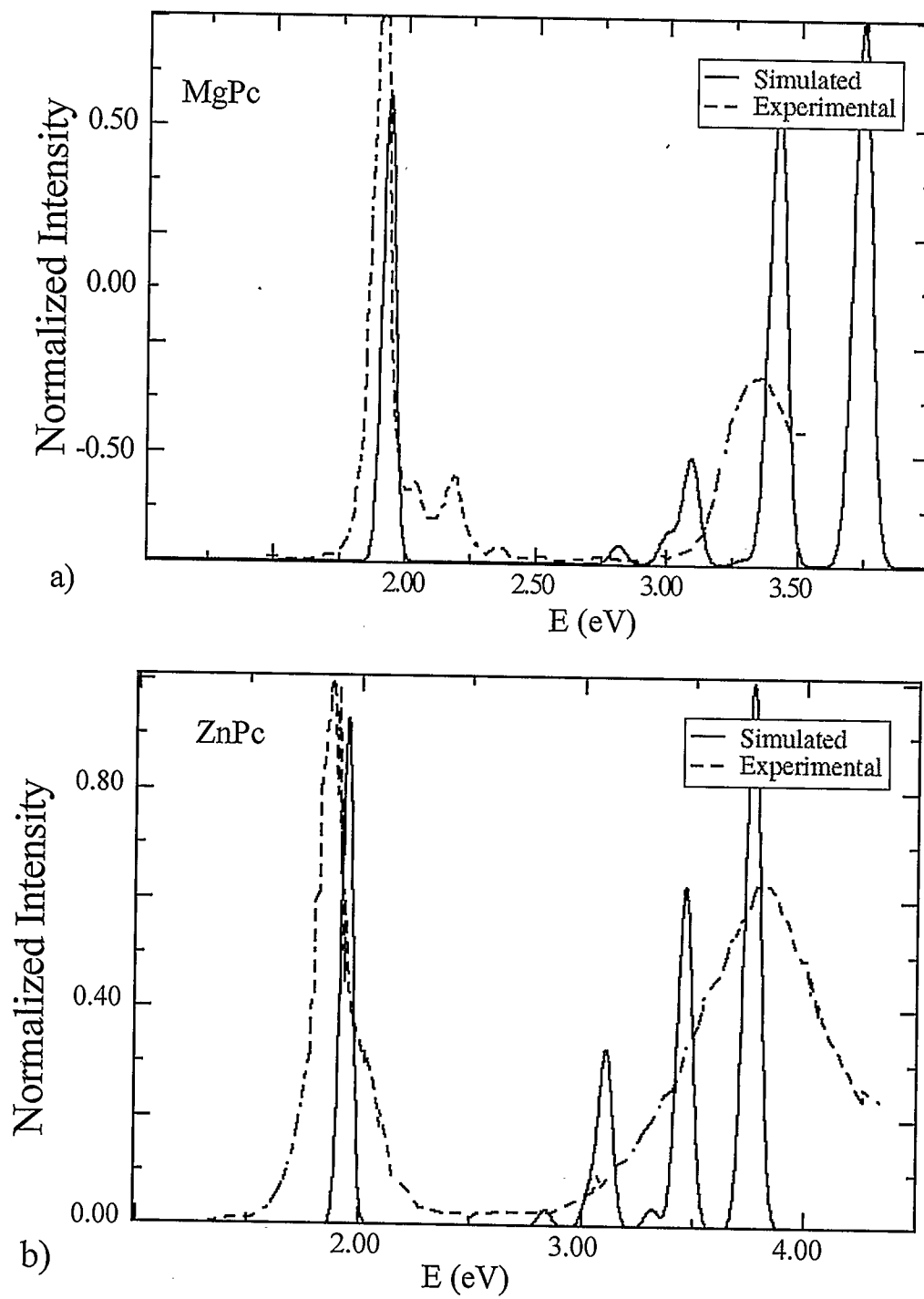


Figure 4.14. Experimental UV-Vis absorption spectra corresponding to a) MgPc [84] and b) ZnPc(-2)Im₂ [82].

5. CONCLUSIONS

A set of simple yet useful equations has been derived for the first time allowing complete description and assignment of the different bands observed in the MCD spectra of porphyrins and derivatives (closed-shell) for different ligand/metal combinations. Mg, Ni and Zinc were studied in combination with ligands such as TPP, OEP, TAP and Pc. These complexes were described and compared with well characterized and described systems obtaining results similar to those reported experimentally. The derived equations were also applied to more controversial systems affording the full description of the Q and B bands. It was then demonstrated that to fully describe the MCD spectra of these complexes both A and B terms must be taken into account, specifically when describing the Soret region instead of just using B -terms as it has been proposed before. In general it was found that the Q band of porphyrins and derivatives are dominated by an A -term while the Soret band region depends on the interaction of A and B terms. This study also singled out the relevant orbitals involved in the observation of the Q and B bands of the studied complexes and follows how they are influenced by geometry changes. Results were compared with experimental data, when available, with excellent agreement (except in the MgOEP and ZnOEP cases). This work also covered the influence of geometry distortions on the studied systems demonstrating that the overall shape of the MCD spectra is not affected (when considering $Q(0,0)$ and $B(0,0)$). Vibronic coupling was not included in our simulations and it could be of interest to explore this area in the future. Furthermore, the recent implementation of open-shell MCD calculation capabilities in ADF also opens another interesting area of research. In spite of being a simple model and

making use of several approximations, the formalism allows for the description and assignment of the MCD spectra of a wide range of porphyrins and porphyrin derivatives opening new research possibilities in this field.

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