

Magnetic Circular Dichroism of Porphyrins Containing M = Ca, Ni, and Zn. A Computational Study Based on Time-Dependent Density Functional Theory

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A theoretical study is presented on the magnetic circular dichroism (MCD) exhibited by the porphyrin complexes MP (M = Mg, Ni, Zn), MTPP (M = Mg, Ni, Zn), and NiOEP, where P = porphyrin, TPP = tetraphenylporphyrin, and OEP = octaethylporphyrin. The study makes use of a newly implemented method for the calculation of \mathcal{A} and \mathcal{B} terms from the theory of MCD and is based on time-dependent density functional theory (TD-DFT). It is shown that the MCD spectrum is dominated by a single positive \mathcal{A} term in the Q-band region in agreement with experiment where available. The band can be fully explained as the first transition in Gouterman's four-orbital model for the type of porphyrins studied here. For the Soret band, the experimental MCD spectrum appears as a single positive \mathcal{A} term. This is also what is found computationally for NiP and NiTPP, where the second transition in Gouterman's four-orbital model give rise to a positive \mathcal{A} term. However, for the remaining systems, the simulated MCD spectrum is actually due to two \mathcal{B} terms that have the appearance of one positive pseudo \mathcal{A} term. The two \mathcal{B} terms appear because the second Gouterman state is coupled strongly to a second excited state ($b_{2u} \rightarrow 2e_g$) of nearly the same energy by the external magnetic field.

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 complexes. Until now, many studies have been carried out at the semiempirical, DFT, and ab initio levels on the electronic spectra of porphyrin complexes,^{5–12} including one *PPP-CI* study of the MCD spectra of these molecules.¹³ The MCD

spectra of porphyrins have also been analyzed by semiempirical 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 pointing in the direction of the propagating light. MCD is the most important of the magneto optical activity techniques and allows for the characterization of excited and ground state symmetries. The fact that all of the substances are MCD active makes it an attractive technique, and it has found many applications in the description of biological systems.^{16–18} MCD theory is well established, and further details can be

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found in references.^{17,19–33} Porphyrin complexes play an important role in biological processes as diverse as respiration and photosynthesis. 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,^{40–46} photonics,^{40–44} and catalysis.^{47–48} 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 of the experimental and theoretical studies, some aspects of the MCD spectra of porphyrins and derivatives are still not well understood, especially the relative contributions from \mathcal{A} and \mathcal{B} terms. 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 the section on the Theoretical Method and Computational Details. After that, we review first in Results and Discussion, the essential features of the molecular orbital level diagrams for porphyrins in conjunction with their recorded absorption UV spectrum. In the last part of Results and Discussion, we present the simulated MCD spectra and compare them to experimental results for porphyrins. On the basis of these comparisons, we finally comment on previously published assignments of the Q and Soret bands. The systems investigated here include the simple porphyrins MgP, ZnP, NiP, as well as MgTPP, ZnTPP, NiTPP (TPP = Tetraphenylporphyrin), and NiOEP (OEP = Octaethylporphyrin).

2. Theoretical Method and Computational Details

2.1. Details of the Calculations. All of the calculations were based on the Amsterdam program package ADF and its implementation of the time-dependent density functional theory (TD-DFT).^{56–59} The molecular structures were optimized based on the BP86 functional due to Becke⁶⁰ and Perdew.⁶¹ The simulation of all of the 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

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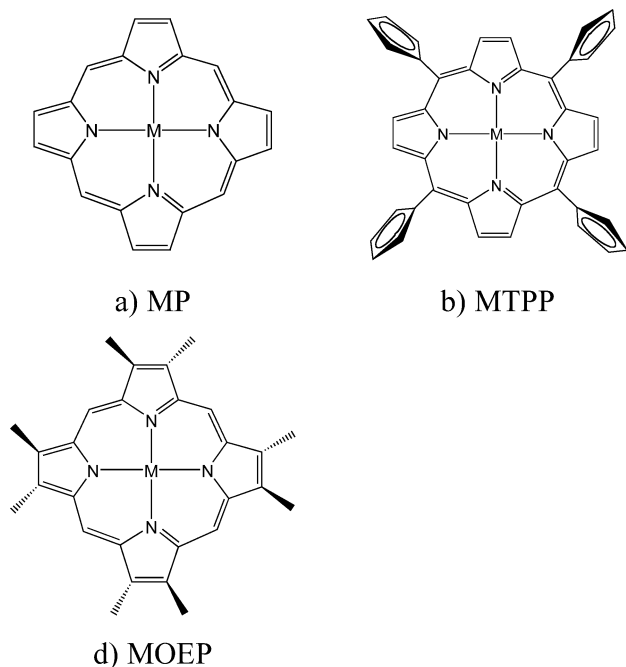


Figure 1. Studied complexes: (a) porphyrin, (b) tetraphenylporphyrin, and (c) octaethylporphyrin.

All of the symmetry and spin allowed transitions from the singlet $^1A_{1g}$ ground state to the singlet $^1A_{2u}$ and 1E_u excited states were calculated in the range of 2–6 eV. We shall, in the following for the sake of brevity, omit the superscript because only singlet states are involved in our discussion. 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 of the elements. The core shells $1s^2$ of carbon, nitrogen, $1s^2 2s^2 2p^6$ of magnesium, and $1s^2 2s^2 2p^6 3s^2 3p^6$ of nickel and zinc were frozen. A set of single- ζ STO polarization functions were used as follows: 2p, 3d for hydrogen; 3d, 4f for carbon and nitrogen; 3p, 3d, and 4f for magnesium; 4s, 4p, and 4f for nickel; and 4p and 4f for zinc. The symmetry was assumed to be D_{4h} for the studied molecules except for the octaethylporphyrin, where a D_{2d} symmetry was used. Figure 1 displays the three different ligands studied. The routines used to calculate the angular momentum integrals required in this study were introduced in connection with the implementation of a method for the calculation of the Verdet constant.^{4c}

2.2. Magnetic Circular Dichroism. In MCD, we consider a sample perturbed by a homogeneous magnetic field \vec{B} of field strength B . For this sample, we measure the difference between its molar extinction coefficient¹⁹ ϵ of left ($\epsilon_-(\omega)$) and right ($\epsilon_+(\omega)$) circular polarized light propagating in the direction of the magnetic field with the angular frequency ω divided by $\hbar\omega$.¹⁹ The difference is after averaging the orientation of the molecules in the sample relative to the direction of the magnetic field given by^{19b}

$$\frac{\epsilon_-(\omega) - \epsilon_+(\omega)}{\hbar\omega} = \frac{\Delta\epsilon}{\hbar\omega} = \lambda_0 \mu_B \left(\sum_J - \mathcal{A}_{AJ} \frac{\partial \rho_{AJ}(\omega)}{\partial \omega} + \left(\mathcal{B}_{AJ} + \frac{C_{AJ}}{kT} \right) \rho_{AJ}(\omega) \right) B \quad (1)$$

where:^{19c}

$$\lambda_0 = \frac{2N_0 \pi^3 \vartheta^2 \log e}{250hcn} \quad (2)$$

Here, ϑ is a proportionality constant that relates the macroscopic electric field of the incident light with the corresponding microscopic field experienced by the molecule, $\rho_{AJ}(\omega)$ is the density of states function for the transition from the ground state (A) to an excited state (J) as a function of the angular frequency of light ω . Further, h is the Planck constant, c is the speed of light, n is the refractive index, N_0 is Avogadro's number, and μ_B is the Bohr magneton. In our simulations, use is made of a Gaussian band-shape function $f_j(\omega)$ in place of $\rho_{AJ}(\omega)$, where

$$f_j(\hbar\omega) = \frac{1}{\Omega_J \sqrt{\pi}} \exp[-(\hbar\omega - \hbar\omega_J)^2 / \Omega_J^2] \quad (3)$$

and $W_J = \hbar\omega_J$ is the energy of the excited state J relative to the ground state A . Further, Ω_J is a bandwidth parameter taken from experimental spectra. A useful empirical relation is $\Omega_J = 0.08\sqrt{W_J}$ with W_J in eV.

The \mathcal{A} -term parameter \mathcal{A}_{AJ} in eq 1 represents a contribution to $\Delta\epsilon(\omega)$ for systems that have degeneracies in the ground state, the excited state, or in both. The magnetic field can split the degenerate states in such a way that it leads to a difference in the absorption of left- and right-polarized light¹⁹ at the absorption frequency ω . The \mathcal{A} -term parameter \mathcal{A}_{AJ} is given by^{19d}

$$\mathcal{A}_{AJ} = \frac{i}{3|A|} \sum_{\alpha} \sum_{\alpha'} \sum_{\lambda} \sum_{\lambda'} (\langle J\lambda | \hat{L} | J\lambda' \rangle \delta_{\alpha\alpha'} - \langle \alpha\alpha' | \hat{L} | \alpha\alpha' \rangle \delta_{\lambda\lambda'}) (\langle \alpha\alpha' | \hat{M} | J\lambda \rangle \times \langle J\lambda' | \hat{M} | \alpha\alpha' \rangle) \quad (4)$$

Here, α is a component of the possibly degenerate ground state, and λ is a component of the possibly degenerate excited state. Further, “ \cdot ” represents a scalar vector product and “ \times ” a “cross” vector product. In addition, $|A|$ is the total degeneracy of the ground state with a value of one for the current systems. Also, \hat{L} is the dimensionless total angular momentum operator in which \hbar has been omitted. Thus,

$$\hat{L} = \sum_{j=1}^n \hat{l}_j = -i \sum_{j=1}^n \vec{r}_j \times \vec{\nabla}_j \quad \hat{M} = \sum_{j=1}^n \hat{m}_j = -i \sum_{j=1}^n \vec{r}_j \times \vec{\nabla}_j \quad (5)$$

where \hat{l}_j is the operator for the dimensionless one-electron orbital angular momentum. A Cartesian component of \hat{l}_j is written as $\hat{l}_{j,\mu}$, or in brief form \hat{l}_μ . On the other hand, \hat{M} is the total electronic dipole operator.

$$\hat{M} = \sum_{j=1}^n \hat{\mu}_j \quad (6)$$

where $\hat{\mu}_j = -\vec{r}_j$ is the one-electron electric dipole operator in atomic units. A Cartesian component of $\hat{\mu}_j$ is written as $\hat{\mu}_{j,\mu}$, or in brief form $\hat{\mu}_\mu$.

The \mathcal{B} -term parameter \mathcal{B}_{AJ} in eq 1 is given by^{19d}

$$\mathcal{B}_{AJ} = \text{Im} \left\{ \frac{2}{3|A|} \sum_{\alpha} \sum_{\lambda} \sum_{K \neq A} \sum_{\kappa} \frac{\langle K\kappa | \hat{L} | \alpha\alpha \rangle}{W_K - W_A} \langle \alpha\alpha | \hat{M} | J\lambda \rangle \times \langle J\lambda | \hat{M} | K\kappa \rangle \right\} + \text{Im} \left\{ \frac{2}{3|A|} \sum_{\alpha} \sum_{\lambda} \sum_{K \neq J} \sum_{\kappa} \frac{\langle J\lambda | \hat{L} | K\kappa \rangle}{W_K - W_J} \langle \alpha\alpha | \hat{M} | J\lambda \rangle \times \langle K\kappa | \hat{M} | \alpha\alpha \rangle \right\} \quad (7)$$

This term represents the contribution to $\Delta\epsilon(\omega)$ from the mixing of the ground state A with all other excited states K as a result of the external homogeneous magnetic field \vec{B} , as well as the mixing induced by \vec{B} between J and all other excited states K with possible

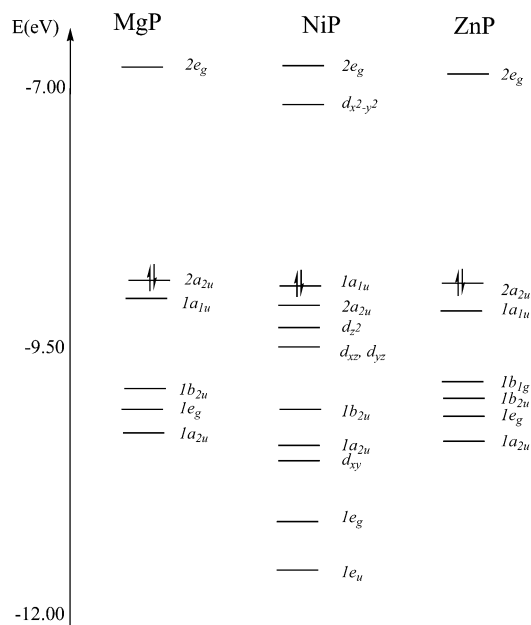


Figure 2. Molecular Orbital energy-levels diagram corresponding to MP.

degenerate components κ . Further, W_A , W_J , W_K are the energies of the states A , J , and K , respectively. The strength of the external magnetic field is indicated by B .

The last parameter^{19d} C_{AJ} in eq 1 is of importance for systems with degenerate ground states where the population of the different components α in the presence of \vec{B} might differ as a function of T . The variation in the population with T will give a temperature-dependent contribution to $\Delta\epsilon(\omega)$. This C term will not be of importance in the present study involving porphyrins with a closed-shell ground state and is not discussed any further here.¹⁹ The expressions^{19d} for \mathcal{A} , \mathcal{B} , and \mathcal{C} are applicable for closed-shell molecules. For open shell molecules,¹⁹ one has to add the dimensionless operator $2\hat{S}$ to \hat{L} in the expressions for \mathcal{A} , \mathcal{B} , and \mathcal{C} , where \hat{S} is the many-electron spin operator where \hbar has been omitted. Thus, the matrix elements in eqs 3–5 containing \hat{L} , or in the general case $\hat{L} + 2\hat{S}$, are all dimensionless.

We finally have for the dipole strength averaged over all orientations.

$$\mathcal{D}_{AJ} = \frac{1}{3|A|} \sum_{\alpha,\lambda} |\langle A_\alpha | \hat{M} | J_\lambda \rangle|^2 \quad (8)$$

We refer to the literature for the way in which time-dependent density functional theory (TD-DFT)^{65–66} is used to evaluate the \mathcal{A} ,^{4a} \mathcal{B} ,^{4d} \mathcal{C} ,^{4b–4c} and \mathcal{D} ⁵⁶ terms.

3. Results and Discussion

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. A very interesting review on this subject has recently been published by Baerends et al.¹² The orbital levels for the systems discussed here are shown in Figures 2 (MP) and 3 (MTPP + ZnOEP). The shape of the orbitals are given in Figure 4.

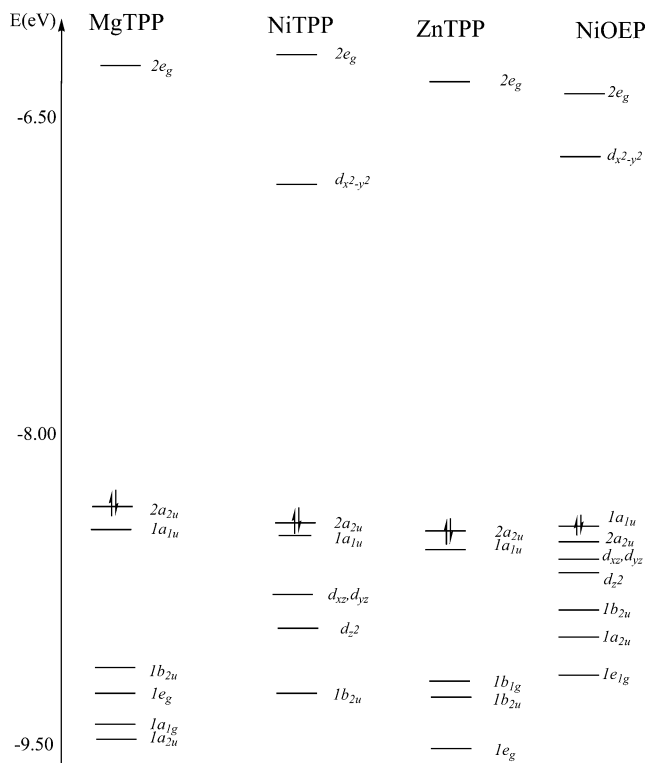


Figure 3. Molecular orbital energy-levels diagram for MTPP and NiOEP.

3.1. Orbital Levels in MP, MTPP, and MOEP. Two of the three types of complexes (MP and MTPP) studied here were considered to have a D_{4h} symmetry, in line with previous experimental and theoretical works. On the other hand, ZnOEP was considered to have D_{2d} symmetry. We have, for simplicity, labeled the orbital levels according to D_{4h} even for NiOEP. All of the complexes were placed in the XY plane with the C_4 axis pointing in the z direction.

We found for all of the systems the lowest-unoccupied ligand-based level to be 2-fold degenerate and represented by a set of π^* orbital of e_g symmetry (Figures 2 and 3). The two occupied levels of highest energy are nearly degenerate and represented by π^* orbital of a_{2u} and a_{1u} symmetry (Figures 2 and 3).

It follows from the level diagrams in Figures 2–3 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. Nevertheless, complexes containing a nickel 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 (Figure 2 for NiP). The empty d-based orbital of b_{1g} symmetry has a 57% contribution from $d_{x^2-y^2}$, whereas the highest-occupied d level of a_{1g} symmetry has a contribution of 89% d_z^2 . The next doubly degenerate $1e_g$ level is represented by two orbitals that have a contribution of 57% from the d_{yz} and d_{xz} , respectively, whereas the lowest d level belonging to the b_{2g} representation has a 92% contribution from the d_{xy} . Of all the mentioned d

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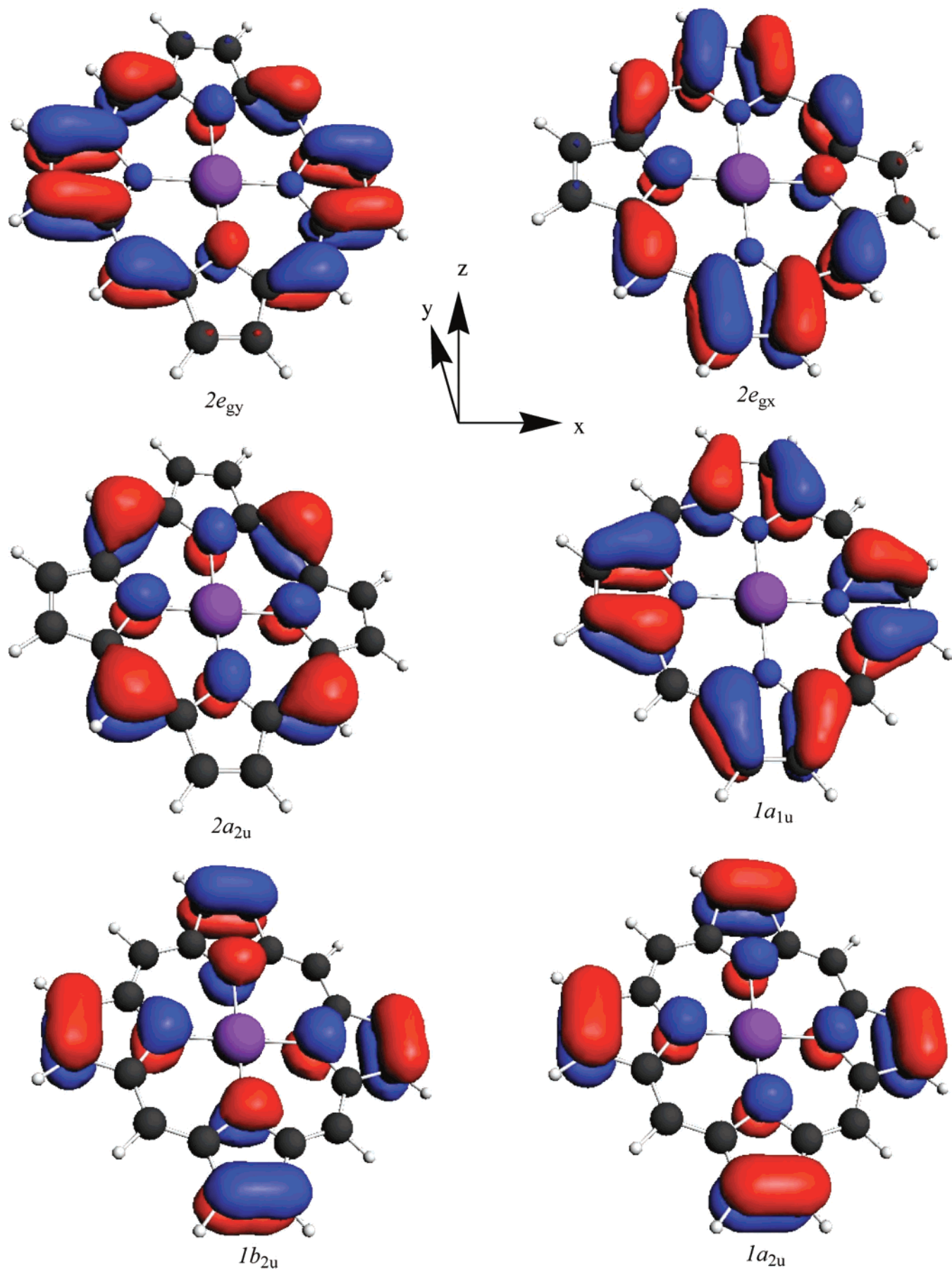


Figure 4. Most important ligand orbitals for porphyrin systems.

orbitals, the $d_{x^2-y^2}$ is of special importance because it is involved actively in transitions located in the B band. We indicate the d levels in Figures 2–3 in terms of $d_{x^2-y^2}$, d_{z^2} , etc., rather than their symmetry labels, b_{1g} , a_{1g} , etc. Furthermore, the d levels were not added to the numbering of the levels ($1e_g$, $2e_g$, etc.), 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 $M = \text{Ni}$. Also, the two functions spanning the e_g representation transform as d_{yz} and d_{xz} , respectively. We shall in the following refer to them as e_{gx} and e_{gy} .

3.2. General Discussion of the UV–Vis Absorption Spectra of Metal Porphyrins. The absorption spectrum of metal porphyrins and their derivatives has been studied extensively by experimental methods. Theoretically, they have 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 because 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 lower-energy Q and Soret bands.

The only dipole and spin allowed transitions from the A_{1g} singlet ground state are to the nA_{2u} and nE_u singlets, of which only the $A_{1g} \rightarrow nE_u$ transitions are observed in the absorption spectra. The oscillator strength of the $A_{1g} \rightarrow nA_{2u}$ transitions is very close to zero in the experimental range, so the absorption spectra will be dominated by transitions of the former type.^{4,69–70}

The band of lowest energy in the absorption spectra of a metal porphyrin or its derivatives is termed the Q band. It consists in the MP, MTPP, and MOEP systems of one transition made up of two one-electron excitations from occupied orbitals of $1a_{1u}$ and $1a_{2u}$ symmetries, respectively, to the $2e_g$ LUMO. In MP (and to a somewhat lesser degree in the MTPP and MOEP systems), the a_{1u} and a_{2u} orbitals (Figures 2 and 3) are nearly degenerate for reasons explained by Gouterman,^{49–55} and $a_{1u} \rightarrow 2e_g$ and $a_{2u} \rightarrow 2e_g$ contribute equally to the transition in the Q band. Furthermore, as shown by Gouterman,^{49–55} the two one-electron excitations have equal contributions of opposite signs to the transition dipole that make the absorption of the Q band weak.

Experimentally, the Soret or B band has been observed to have from one to three sub-bands (B_1 , B_2 , and B_3). The number of resolved bands depends on the complex studied and on the resolution of the spectroscopic technique applied. In our work and in previous studies, one-electron excitation of the type $1a_{1u} \rightarrow 2e_g$ and $1a_{2u} \rightarrow 2e_g$ always contribute with high intensity. Here, $2e_g$ is the unoccupied doubly degenerate level represented by ligand-based orbitals, whereas a_{1u} and a_{2u} are the occupied levels of highest energy

represented by ligand-based orbitals. Additional transitions involve one-electron excitations from the highest-occupied b_{1u} and b_{2u} (Figures 2 and 3) levels representing ligand orbitals to the lowest-unoccupied ligand-based $2e_g$ and b_{1u} levels. It follows from the above discussion that the assignment of the Soret 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. Magnesium, Nickel, and Zinc 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 Magnesium, Nickel, and Zinc Porphyrins. We compare, in this section for the sake of completeness, available experimental UV–vis absorption spectra for metal porphyrins (MP) with theoretical predictions, although such predictions already have been provided and discussed by Baerends¹² et al. An in-depth theoretical analysis of the corresponding MCD spectra will be introduced in the following sections.

The experimental absorption spectra for the three MP systems exhibit two bands in the Q region and a single more-intense band in the Soret region of their UV–vis absorption spectra. The bands in the Q band have been attributed, by experimentalists, to the same electronic transition 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 transition in the experimentally observed range for the Q band.

The Q band of ZnP has been observed from 2.03 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 1). The Q band of MgP has been observed at 2.14 and 2.20 eV, and the Soret band is located^{75,76} at 3.18 eV. NiP has a slight shift to the blue in the Q band (2.28 eV), whereas the Soret band is observed⁷⁵ at 3.18 eV (Table 1). For the porphyrin complexes, the NiP has the highest-calculated Q-band oscillator strength of 0.006, whereas MgP and ZnP were calculated to both be 0.001.

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

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Table 1. Calculated Transition Energies (eV), Oscillator Strength (f), \mathcal{A} , \mathcal{A}/\mathcal{D} , \mathcal{B} , and \mathcal{B}/\mathcal{D} Parameters for MP (M = Mg, Ni, Zn)

complex	symmetry	Exc. Energ. (eV)		composition	%	f	A^h	A/D	B^h	B/D^h	assign.	
		exp	calcd									
MgP	1E _u	2.14 ^a , 2.2 ^b	2.23	2a _{2u} → 2e _g	54.15	0.001	0.01	5.46	-1.25	-6.29 × 10 ²	Q	
			2.23	1a _{1u} → 2e _g	44.58							
	2E _u	3.18 ^a	3.23	1b _{2u} → 2e _g	75.02	0.383	-2.91	-1.80	-3.18 × 10 ³	-1.97 × 10 ³		
			3.30	1a _{1u} → 2e _g	14.11							
	3E _u			3.30	2a _{2u} → 2e _g	6.69			0.43	4.28 × 10 ³		1.07 × 10 ³
				3.30	1a _{1u} → 2e _g	28.98	0.972	1.72				
3.30				2a _{2u} → 2e _g	28.63							
NiP	1E _u	2.28 ^a	2.37	1a _{1u} → 2e _g	50.56	0.006	0.19	5.48	0.97	27.2	Q	
			2.37	2a _{2u} → 2e _g	48.24							
	A _{2u}	3.18 ^a	2.98	1b _{2u} → d _{x²-y²}	99.89	0.000	0.00	0.00	-0.35	-4.69 × 10 ²	B ^g	
			3.21	2a _{2u} → 2e _g	43.17	1.042	1.38	0.31	1.56 × 10 ²	35.4		
	2E _u			3.41	1a _{1u} → 2e _g	41.94						
				3.41	1e _u → d _{x²-y²}	7.23						
3E _u			3.41	1b _{2u} → 2e _g	96.02	0.000	-9.57 × 10 ⁻⁵	-2.75	-0.62	-1.78 × 10 ⁴		
			3.41	1e _g → 1b _{1u}	1.40							
ZnP	1E _u	2.03, ^c 2.21, ^d 2.23, ^e 2.18 ^f	2.28	2a _{2u} → 2e _g	52.10	0.001	0.05	5.49	-1.30	-1.38 × 10 ²	Q	
			2.28	1a _{1u} → 2e _g	46.63							
	2E _u	2.95, ^c 3.09, ^d 3.18, ^e 3.13 ^f	3.25	1b _{2u} → 2e _g	68.44	0.496	-3.37	-1.62	-3.69 × 10 ³	-1.78 × 10 ³	B ^g	
			3.32	1a _{1u} → 2e _{1g}	17.54							
	3E _u			3.32	2a _{2u} → 2e _g	10.05						
				3.32	1b _{2u} → 2e _g	29.88	0.943	-0.57	-0.15	4.57 × 10 ³	1.18 × 10 ³	
3.32				2a _{2u} → 2e _g	29.31							
3E _u			3.32	1a _{1u} → 2e _g	27.13							
			3.32	1a _{2u} → 2e _g	10.30							

^a Ref 69. ^b Ref 71. ^c Ref 70. ^d Ref 72. ^e Ref 73. ^f Ref 74. ^g B band = Soret band. ^h Atomic units.

3.3.2. Detailed Theoretical Discussion of the MCD Band Parameters \mathcal{A} and \mathcal{A}/\mathcal{D} in Magnesium, Nickel, and Zinc Porphyrins.

The metal porphyrins investigated here have a nondegenerate A_{1g} ground state, which precludes C terms in the MCD spectra. On the other hand, the presence of degenerate E_u excited states is likely to give rise to \mathcal{A} terms in the MCD spectra due to the A_{1g} → E_u transitions, and we shall, in the following, give a detailed discussion of the \mathcal{A} terms for porphyrins. \mathcal{B} terms, that are always possible, will be discussed later. The Q band, as seen in Table 1, always consists of excitations from 1a_{1u} and 2a_{2u} orbitals to 2e_g orbitals, whereas the Soret band also includes excitations from 1a_{2u} and 1b_{2u} to 2e_g. The main difference here for the various metal centers (M = Mg, Ni, Zn) is the relative weight by which the one-electron excitations contribute to the Q and Soret bands. A general expression for the \mathcal{A}/\mathcal{D} parameter for these systems is readily obtained from eqs 4 and 8 as:^{4a}

$$\frac{\mathcal{A}}{\mathcal{D}} = -\text{Im} \langle \Psi(1E_{ux}) | \hat{L}_z | \Psi(1E_{uy}) \rangle \quad (9)$$

where 1E_{ux} and 1E_{uy} are the excited states involved in the Q and Soret-band transitions.

As stated before, only one-electron excitations of the kind a_{1u} → 2e_g and a_{2u} → 2e_g contribute to the Q band, so we can express the states of eq 9 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 excitation b_{2u} → 2e_g contributes to the Soret

band. To obtain a generalized equation for the Q and Soret bands of porphyrins, all of the orbitals involved in the transitions in question will be taken into account. Eqs 10 and 11 express $\Psi(1E_{ux})$ and $\Psi(1E_{uy})$ respectively, in terms of the orbitals involved in the one-electron excitations (Table 1).

$$\begin{aligned} \Psi(E_{ux}) = & c_1 \left(\frac{1}{\sqrt{2}} \left| 1a_{1u}^+ 2e_{gx}^- \right| - \frac{1}{\sqrt{2}} \left| 1a_{1u}^- 2e_{gx}^+ \right| \right) + \\ & c_2 \left(\frac{1}{\sqrt{2}} \left| 2a_{2u}^+ 2e_{gy}^- \right| - \frac{1}{\sqrt{2}} \left| 2a_{2u}^- 2e_{gy}^+ \right| \right) + \\ & c_3 \left(\frac{1}{\sqrt{2}} \left| 1b_{2u}^+ 2e_{gy}^- \right| - \frac{1}{\sqrt{2}} \left| 1b_{2u}^- 2e_{gy}^+ \right| \right) + \\ & c_4 \left(\frac{1}{\sqrt{2}} \left| 1a_{2u}^+ 2e_{gy}^- \right| - \frac{1}{\sqrt{2}} \left| 1a_{2u}^- 2e_{gy}^+ \right| \right) \quad (10) \end{aligned}$$

$$\begin{aligned} \Psi(E_{uy}) = & c_1 \left(\frac{1}{\sqrt{2}} \left| 1a_{1u}^+ 2e_{gy}^- \right| - \frac{1}{\sqrt{2}} \left| 1a_{1u}^- 2e_{gy}^+ \right| \right) - \\ & c_2 \left(\frac{1}{\sqrt{2}} \left| 2a_{2u}^+ 2e_{gx}^- \right| - \frac{1}{\sqrt{2}} \left| 2a_{2u}^- 2e_{gx}^+ \right| \right) + \\ & c_3 \left(\frac{1}{\sqrt{2}} \left| 1b_{2u}^+ 2e_{gx}^- \right| - \frac{1}{\sqrt{2}} \left| 1b_{2u}^- 2e_{gx}^+ \right| \right) - \\ & c_4 \left(\frac{1}{\sqrt{2}} \left| 1a_{2u}^+ 2e_{gx}^- \right| - \frac{1}{\sqrt{2}} \left| 1a_{2u}^- 2e_{gx}^+ \right| \right) \quad (11) \end{aligned}$$

An orbital diagram for MP can be found in Figure 2. Two a_{2u} orbitals are involved, and so the prefix 1 and 2 are used to distinguish them (Table 1 and Figures 2 and 4).

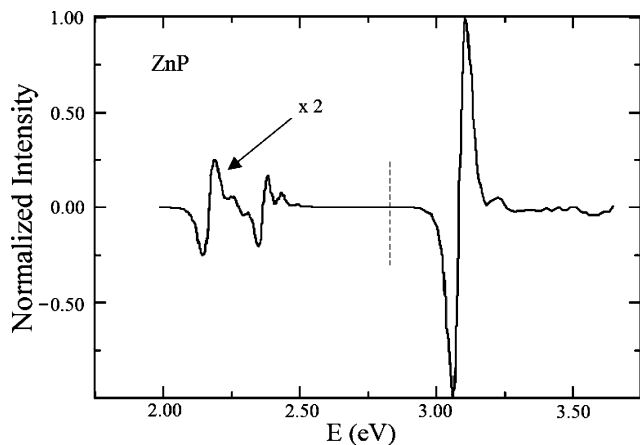


Figure 5. Experimental MCD spectrum for ZnP.

Substituting eqs 10 and 11 into eq 9 affords the general expression 12.

$$\begin{aligned} \frac{\mathcal{A}}{\mathcal{D}} &= -\text{Im}((c_1^2 + c_2^2 - c_3^2 + c_4^2)\langle 2e_{gx} | \hat{l}_z | 2e_{gy} \rangle - \\ &\quad 2c_1c_2\langle 1a_{1u} | \hat{l}_z | 2a_{2u} \rangle - 2c_1c_4\langle 1a_{1u} | \hat{l}_z | 1a_{2u} \rangle) \\ &= T_1 + T_2 + T_3 \end{aligned} \quad (12)$$

A similar analysis of the MCD spectrum of zinc phthalocyanine in terms of eq 12 has previously been given by VanCott et al.²⁰

3.3.3. Simulation of the MCD Spectra for MP based on the \mathcal{A} Term alone. We shall now try to simulate the MCD spectra for the MP systems based solely on calculated \mathcal{A} -term parameters. For the three porphyrin systems MP (M = Zn, Mg, Ni), we calculate positive \mathcal{A} - and \mathcal{AD} -term parameters for the Q band (Table 1). This is in agreement

with the available experimental data limited to ZnP. Thus, Keegan⁷⁷ et al. report a value of 4.2 for \mathcal{AD} , which is in reasonable agreement with our estimate of 5.49. We note again that the experimental MCD spectrum for ZnP exhibits two \mathcal{A} terms in the Q-band region, Figure 5, due to vibronic coupling, whereas only one positive \mathcal{A} band is present in our simulation where vibronic coupling is neglected (Figure 6).

The positive value calculated for the \mathcal{AD} parameter of the Q band can be understood by noting that the corresponding excited state ($1E_u$) in agreement with the four-orbital model of Gouterman^{49–55} can be described by the wave functions in eqs 10 and 11, where $c_1 \sim c_2 \sim 1/\sqrt{2}$, whereas $c_3 = c_4 = 0$. As a consequence, only the first two terms ($T_1 + T_2$) in eq 12 will contribute to the numerical value of \mathcal{AD} . The term $T_1 = -(c_1^2 + c_2^2 - c_3^2 + c_4^2)\text{Im}\langle 2e_{gx} | \hat{l}_z | 2e_{gy} \rangle$ will contribute with a positive value because $\text{Im}\langle 2e_{gx} | \hat{l}_z | 2e_{gy} \rangle$ is negative (Table 2). The contribution from $T_2 = 2c_1c_2\text{Im}\langle a_{1u} | \hat{l}_z | 2a_{2u} \rangle$ is also positive due to the positive sign of $\text{Im}\langle a_{1u} | \hat{l}_z | 2a_{2u} \rangle$.

Turning next to the Soret band, we note that in the Gouterman model $c_1 = -c_2 = 1/\sqrt{2}$ for the second conjugated state ($2E_u$). As a consequence of eq 12, a small positive value of \mathcal{AD} would be predicted as $\text{Im}\langle e_{gx} | \hat{l}_z | e_{gy} \rangle$ numerically is larger than $\text{Im}\langle a_{1u} | \hat{l}_z | 2a_{2u} \rangle$, in Table 2, and T_1 and T_2 are of opposite sign.

The Gouterman model applies approximately to NiP, in Table 1, where we find one \mathcal{A} term in the Soret region as a result of the conjugated excited state, $c_1 = -c_2 = 1/\sqrt{2}$, with a small positive value for \mathcal{AD} of 0.31 and an \mathcal{A} term parameter of 1.38 D² at the absorption energy 3.21 eV. At slightly higher energy (3.41 eV), another excited-state of E_u

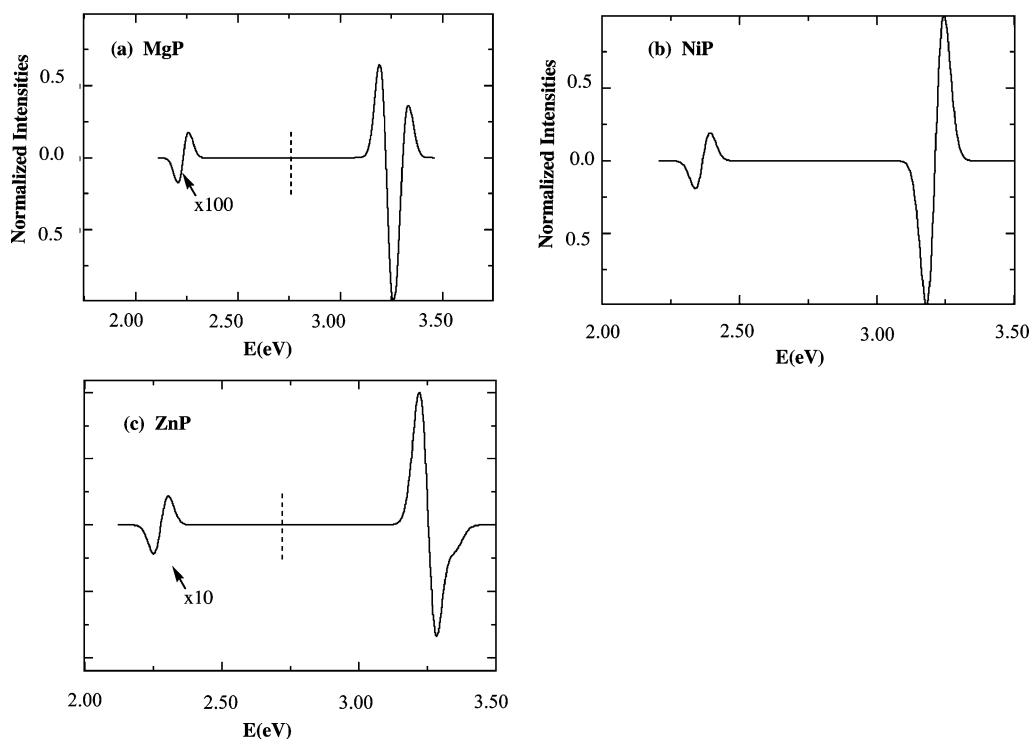


Figure 6. Simulated MCD spectra of MP based on \mathcal{A} terms alone with M = (Mg, Ni, Zn).

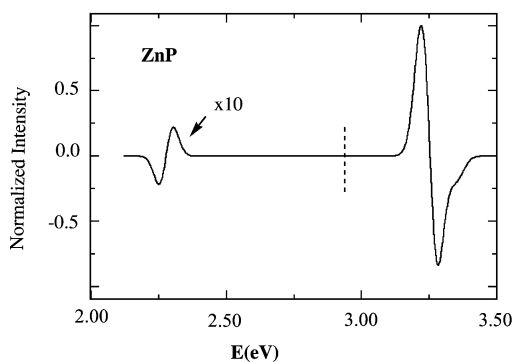


Figure 7. Pseudo \mathcal{A} terms calculated after applying a small geometric perturbation to the ZnP molecule.

Table 2. Angular Momentum Integrals Applied in the Calculation of the \mathcal{AD} Term for the Q and Soret Bands of MP

	Zn	Mg	Ni
$\text{Im}\langle 2e_{gx} \hat{L}_z 2e_{gy}\rangle$	-2.872	-2.881	-2.810
$\text{Im}\langle 1a_{1u} \hat{L}_z 2a_{2u}\rangle$	2.616	2.587	2.651

symmetry ($3E_u$) is found for NiP, and it is entirely due to a $1b_{2u} \rightarrow 2e_g$ one-electron excitation (Table 1). This transition has an \mathcal{AD} value of -2.75 and a small \mathcal{A} -term parameter of $-9.57 \times 10^{-5} D^2$. Thus, the simulated MCD spectrum of NiP in part b of Figure 6 based on only the \mathcal{A} term exhibits a single band with a positive \mathcal{AD} value in the Soret region.

Applying the Gouterman model to $2E_u$ of MgP and ZnP with $c_1 = -c_2 = 1/\sqrt{2}$ in the Soret region would also lead to one \mathcal{A} term in the Soret region, with a small positive \mathcal{AD} value if use is made of the $\text{Im}\langle 2e_{gx}|\hat{L}_z|2e_{gy}\rangle$, $\text{Im}\langle 1a_{1u}|\hat{L}_z|2a_{2u}\rangle$, and $\text{Im}\langle 1a_{1u}|\hat{L}_z|1a_{2u}\rangle$ values reported in Table 2. Likewise, a transition of higher energy involving the $1b_{2u} \rightarrow 2e_g$ one-electron excitation ($3E_u$) would lead to a weak band with a small \mathcal{A} term ($\sim 10^{-3} D^2$). Such a picture is not in agreement with the experimental observation because the recorded MCD spectrum, Figure 5, exhibits a single positive \mathcal{A} -like term in the Soret-band region.

In our calculations, the conjugated second Gouterman excited state $2E_u$ with ($c_1 = -c_2 = 1/\sqrt{2}$) is very close to $3E_u$ ($1b_{2u} \rightarrow 2e_g$, $c_3 \cong 1$) for $M = \text{Zn, Mg}$, with the result that $2E_u$ and $3E_u$ are mixed. The mixing gives rise to a complex-simulated MCD spectrum based on \mathcal{A} terms, alone with a negative \mathcal{A} term followed by a positive \mathcal{A} term in the Soret region of MgP (part a of Figure 6) and two negative \mathcal{A} terms in the Soret-band region in the case of ZnP (part c of Figure 6). The simulated spectrum for ZnP based on \mathcal{A} terms alone (part c of Figure 6) does not agree with the recorded MCD spectrum for ZnP (Figure 5).

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 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 nE_u ($n = 1-3$) excited states into three nearly degenerate pairs (nB_1, nB_2 ; $n = 1-3$), with an energy separation for each pair of $\Delta W_n = W(nB_2) - W(nB_1)$. In planar ZnP, the \mathcal{A} term for each of the three excited states comes from the mixing of the nE_{ux} and nE_{uy} components. In the bent ZnP, we describe the same phenomenon by allowing the magnetic field to mix the nB_1 and nB_2 components with the same n . We thus get, according to the theory outlined in the previous chapter for each $n = 1-3$, two \mathcal{B} terms

$$\mathcal{B}(nB_1) = \text{Im} \left\{ \frac{-2 \langle nB_1|\hat{L}_z|nB_2\rangle \langle A_1|\hat{M}_x|nB_1\rangle \langle nB_2|\hat{M}_y|A_1\rangle}{3 \Delta W_n} \right\} \quad (13)$$

and

$$\mathcal{B}(nB_2) = \text{Im} \left\{ \frac{2 \langle nB_1|\hat{L}_z|nB_2\rangle \langle A_1|\hat{M}_x|nB_1\rangle \langle nB_2|\hat{M}_y|A_1\rangle}{3 \Delta W_n} \right\} \quad (14)$$

that are equal in size but opposite in sign and separated by ΔW_n . They will thus appear in the MCD spectrum as pseudo \mathcal{A} terms.⁷⁸ Figure 7 presents the simulated MCD spectrum based on the three pseudo \mathcal{A} terms. It is clear from a comparison of part c of Figure 6 and Figure 7 that the bend only has a minor influence. Calculations with other values for the bending angle led to a similar conclusion.

3.3.5. Influence of \mathcal{B} Terms on the Simulated MCD Spectra of Planar MP. So far, we have neglected the magnetic coupling between excited states nE_u and pE_u , where n is different from p . Such a coupling gives rise to the general \mathcal{B} -term parameter expressed in eq 7. We get for each of the three excited states nE_u ($n = 1-3$) an associated \mathcal{B} -term parameter given by

$$\mathcal{B}(nE_u) = \text{Im} \left\{ \frac{-4 \sum_{p \neq n} \langle nE_{ux}|\hat{L}_z|pE_{uy}\rangle \langle A_{1g}|\hat{M}_x|nE_{ux}\rangle \langle pE_{uy}|\hat{M}_y|A_{1g}\rangle}{3 [W(pE_{1uy}) - W(nE_{1uy})]} \right\} \quad (15)$$

Figure 8 displays the simulated spectrum due to the \mathcal{B} terms given in eq 15 for all three MP systems. The \mathcal{B} term for $n = 1$ in the Q band is very small due to the large separation between $1E_u$ on the one hand and $2E_u$ and $3E_u$ on the other (Table 1). However, the \mathcal{B} -term parameters for $2E_u$ and $3E_u$ in the Soret region are numerically large and of opposite sign because they are dominated by the magnetic coupling of $2E_u$ and $3E_u$ 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 \mathcal{A} term. The numerical calculation further shows that this pseudo \mathcal{A} term is positive.

When we finally add the \mathcal{A} terms of Figure 6 to the \mathcal{B} terms of Figure 8, we get in Figure 9 a fully simulated MCD

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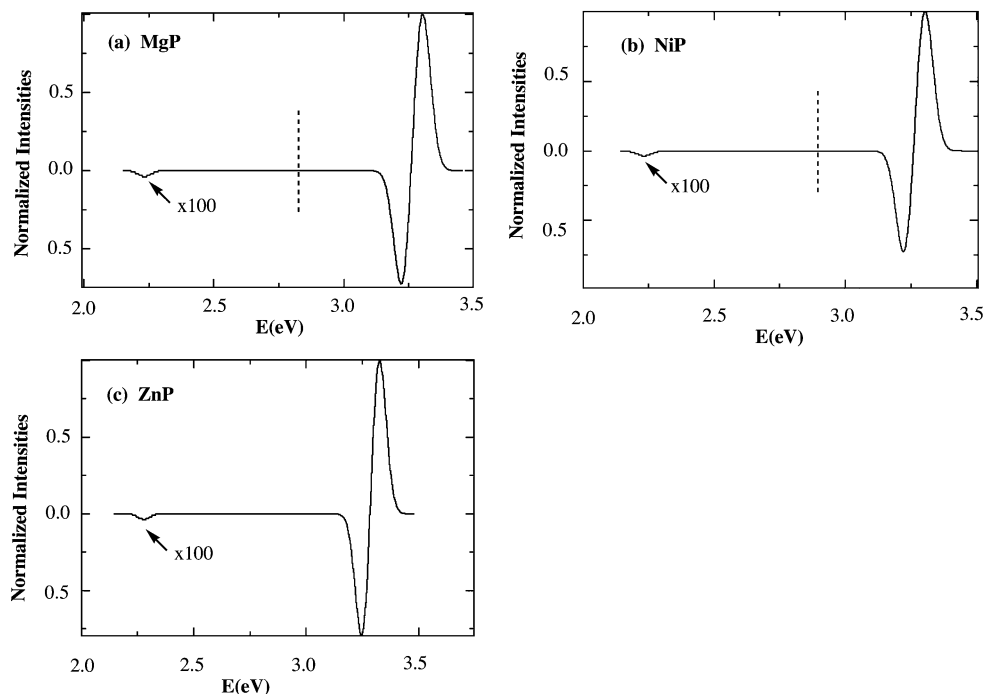


Figure 8. Simulated MCD including only the \mathcal{B} terms due to the mixing of different excited states for the MP systems.

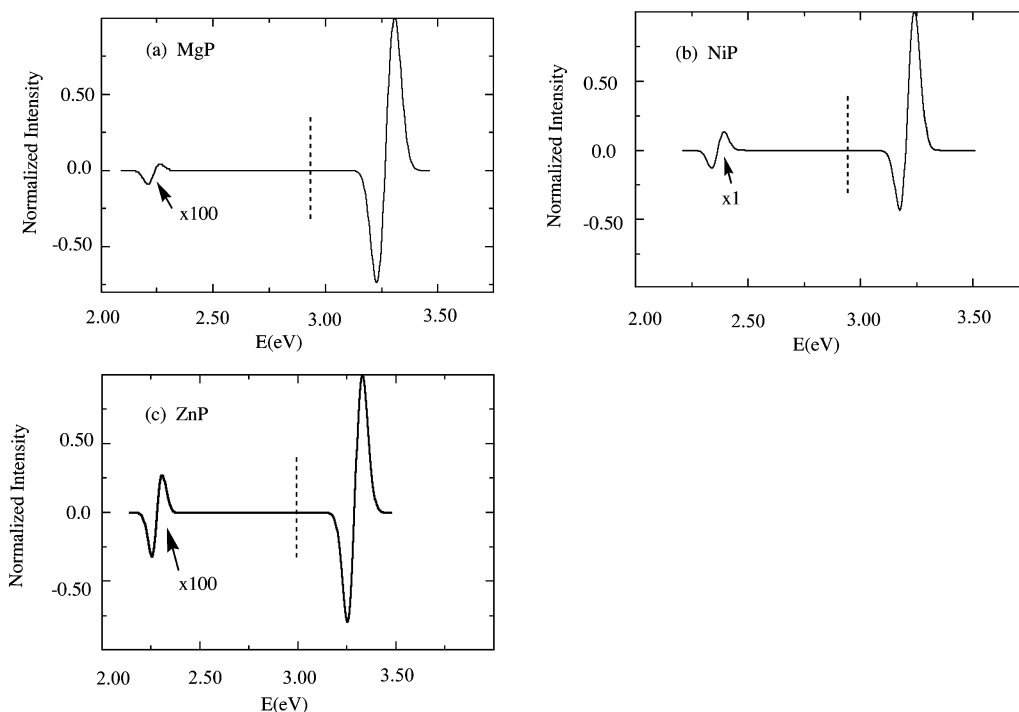


Figure 9. MCD spectra of MP complexes including both \mathcal{A} and \mathcal{B} terms.

spectrum that is quite similar for the three systems and in qualitatively good agreement with experiment for ZnP⁷⁷ (Figure 5). Thus, we now have one dominating positive pseudo \mathcal{A} term due to the magnetic coupling between $2E_u$ and $3E_u$ in the Soret-band region.

3.4. MCD Spectra of MTPP (M = Mg, Ni, Zn) NiOEP.

We shall now turn to a discussion of the MCD spectra of MgTPP, ZnTPP, NiTPP, and ZnOEP. Here, the TPP (tetraphenylporphyrin) and OEP (octaethylporphyrin) ligands are shown in parts b and c of Figure 1, respectively. The

corresponding orbital level diagrams for MTPP (M = Mg, Ni, Zn) and ZnOEP are displayed in Figure 3. For TPP, we have modified the simple porphyrin ligand by replacing a hydrogen in the m position (Figure 10) with a phenyl group (Figure 1). In the case of the OEP ligand, the substitution involves replacing a hydrogen in the β -position (Figure 10) with an ethyl group (Figure 1). Neither of the substitutions are seen to have any significant influence on the relative energies of the higher-unoccupied ($2e_g$) and lower-occupied ($2a_{2u}$, $1a_{1u}$, and $1b_{2u}$) orbitals (Figures 3 and 4).

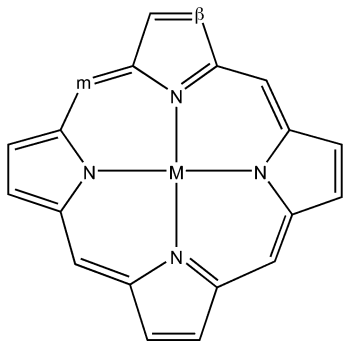


Figure 10. Positions for *m* and β substitution in porphyrin ring.

3.4.1. Detailed Discussion of Simulated MCD Spectra for MTPP and ZnOEP in the Q-Band Region Based on the \mathcal{A} Term Alone. The simulated MCD spectra for the Q band of MTPP (M = Mg, Ni, Zn) and NiOEP based on the \mathcal{A} term alone (Figure 11) are very similar to the corresponding spectra for the pure porphyrins, MP (Figures 6). Thus, MP on the one hand (Tables 1) and MTPP and NiOEP (Tables 3 and 4) on the other exhibit a positive \mathcal{A} term with comparable $\mathcal{A}\mathcal{D}$ values. This is in agreement with experimental data available for NiTPP,⁷⁹ ZnTPP,^{77,80} and NiOEP⁷⁰ (Figures 12, 13, and 14, respectively). Keegan et al.⁷⁷ reported a value of 3.52 for $\mathcal{A}\mathcal{D}$ of ZnTPP compared to the theoretical estimate of 5.17. Although the agreement is reasonable, the calculated value appears to be overestimated. It should be noted that, as in the case of MP, two \mathcal{A} terms are observed experimentally in the Q-band MCD spectra of ZnTPP and NiTPP (Figures 12 and 13). We highlight again that the two experimental \mathcal{A} terms are due to vibronic coupling. Our simulation neglects vibronic coupling, and we find for that reason only a single (positive) \mathcal{A} term in the Q-band region.

As for the MP systems, the first excited state ($1E_u$) in MTPP and NiOEP responsible for the observation of the Q band can be described by the wave functions in eqs 10 and 11 with $c_1 \sim c_2 \sim 1/\sqrt{2}$, in accordance with the Gouterman four-orbital model.^{49–55} Because $c_3 = c_4 = 0$, only the first two terms of eq 12, T_1 and T_2 , will contribute to the final value of $\mathcal{A}\mathcal{D}$. The contribution from T_1 to $\mathcal{A}\mathcal{D}$ is positive because it can only be affected by the sign of the integral $\text{Im}\langle 2e_{gx}|\hat{l}_z|2e_{gy}\rangle$, which is negative. T_2 also contributes with a positive sign because the sign of $\text{Im}\langle 1a_{1u}|\hat{l}_z|2a_{2u}\rangle$ as well as the coefficients in T_2 are positive, Table 5.

3.4.2. Discussion of Simulated MCD Spectra for MTPP in the Soret Region Based on \mathcal{A} Terms Alone. Applying the Gouterman model to the Soret region of the MTPP systems would give $c_1 = -c_2 = 1/\sqrt{2}$ and $c_3 = c_4 = 0$. The use of the Gouterman model gives rise to an intense absorption at the $2E_u$ state of NiTPP with $f = 2.98$ and yields a positive \mathcal{A} -term parameter of 2.19 D² in the Soret region (Figure 11), with a small positive $\mathcal{A}\mathcal{D}$ ratio of 0.33 at the absorption energy of 3.03 eV (Table 3). The calculated positive \mathcal{A} term in the Soret region (Table 3 and Figure 11) is in good agreement with experiment,⁷⁹ where only a single \mathcal{A} term is observed (Figure 12). An additional state ($3E_u$) is calculated at a higher energy (3.28 eV). It is due mainly to the one-electron excitation $1b_{2u} \rightarrow 2e_g$ (Table 3). This transition has a negative \mathcal{A} -term parameter with $\mathcal{A} = -0.18$ D² and $\mathcal{A}\mathcal{D} = -2.64$ (Table 3), similar to the corresponding transition to $3E_u$ in NiP (Table 2). The simulated MCD spectrum for NiTPP based on \mathcal{A} terms alone (Figure 11) reveals, in agreement with experiment (Figure 12), only a single positive \mathcal{A} term as the numerically much smaller negative \mathcal{A} term from $3E_u$ is

Table 3. Calculated Transition Energies (eV), Oscillator Strength (*f*), \mathcal{A} , $\mathcal{A}\mathcal{D}$, \mathcal{B} , and $\mathcal{B}\mathcal{D}$ Parameters for MTPP (M = Mg, Ni, Zn)

complex	symmetry	Exc. Energ. (eV)		composition	%	<i>f</i>	\mathcal{A}^e	\mathcal{A}/\mathcal{D}	\mathcal{B}^e	$\mathcal{B}/\mathcal{D}^e$	assign.	
		exp	calcd									
MgTPP	$1E_u$		2.14	$2a_{2u} \rightarrow 2e_g$	58.00	0.014	0.23	5.14	17.42	3.84×10^2	Q	
					$1a_{1u} \rightarrow 2e_g$	40.81						
	$2E_u$		3.05	$1a_{1u} \rightarrow 2e_g$	43.24	3.302	2.58	0.36	-2.23×10^3	-3.12×10^2	B^d	
					$2a_{2u} \rightarrow 2e_g$	26.35						
					$1b_{2u} \rightarrow 2e_g$	17.09						
	$3E_u$		3.14	$1b_{2u} \rightarrow 2e_g$	80.41	0.754	-3.55	-2.17	3.01×10^3	1.84×10^3		
				$2a_{2u} \rightarrow 2e_g$	7.73							
				$1a_{1u} \rightarrow 2e_g$	5.80							
NiTPP	$1E_u$	1.98 ^a	2.28	$2a_{2u} \rightarrow 2e_g$	52.06	0.901×10^{-4}	2.79×10^3	5.17	0.80	1.50×10^3	Q	
				$1a_{1u} \rightarrow 2e_g$	46.82							
	$1A_{2,u}$		2.89	$1b_{2u} \rightarrow d_{x^2-y^2}$	99.77	0.781×10^{-4}	0.00	0.00	-0.44	-1.20×10^3		
	$2E_u$		2.91 ^a	3.03	$1a_{1u} \rightarrow 2e_g$	44.35	2.98	2.19	0.33	53.07	7.92	B^d
					$2a_{2u} \rightarrow 2e_g$	38.78						
	$3E_u$		3.16	3.16	$1e_u \rightarrow d_{x^2-y^2}$	96.17	0.104	0.02	0.09	0.64	2.87	
$4E_u$		3.28	3.28	$1b_{2u} \rightarrow 2e_g$	95.09	0.034	-0.18	-2.64	19.6	2.80×10^2		
ZnTPP	$1E_u$	2.05, ^b 2.16 ^c	2.19	$2a_{2u} \rightarrow 2e_g$	55.94	0.008	0.13	5.17	10.20	4.14×10^2	Q	
					$1a_{1u} \rightarrow 2e_g$	42.86						
	$2E_u$	2.97, ^b 2.89 ^c	3.07	$1a_{1u} \rightarrow 2e_g$	43.66	3.352	1.94	0.26	-1.92×10^3	-2.58×10^2	B^d	
					$2a_{2u} \rightarrow 2e_g$	29.56						
					$1b_{2u} \rightarrow 2e_g$	15.05						
	$3E_u$		3.15	$1b_{2u} \rightarrow 2e_g$	82.32	0.708	-3.41	-2.24	2.54×10^3	1.67×10^3		
				$2a_{2u} \rightarrow 2e_g$	7.52							
				$1a_{1u} \rightarrow 2e_g$	4.99							

^a Ref 79. ^b Ref 77. ^c Ref 70. ^d B band = Soret band. ^e Atomic units.

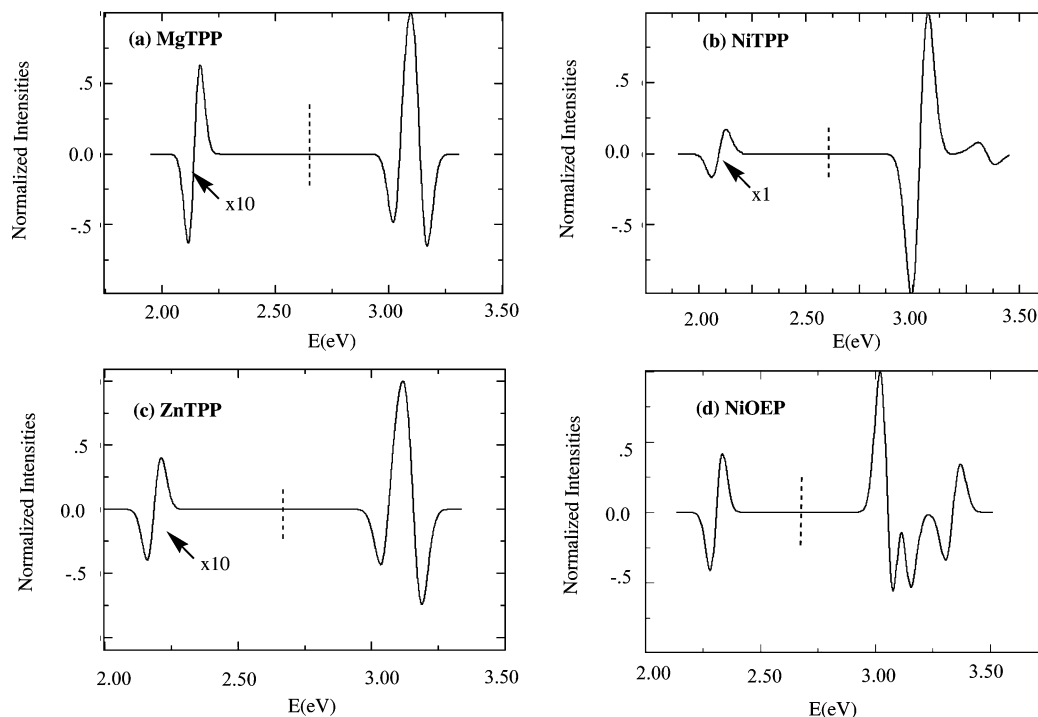


Figure 11. Simulated MCD spectrum of MTTP ($M = \text{Mg}, \text{Ni}, \text{Zn}$) and NiOEP based on \mathcal{A} terms alone.

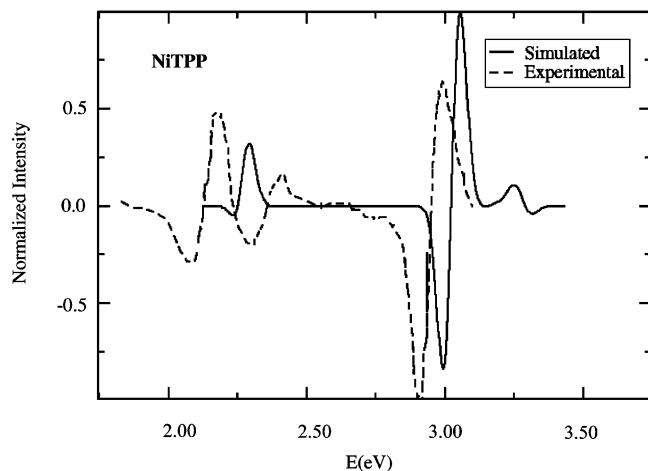


Figure 12. Experimental⁷⁹ and simulated MCD spectra of NiTPP.

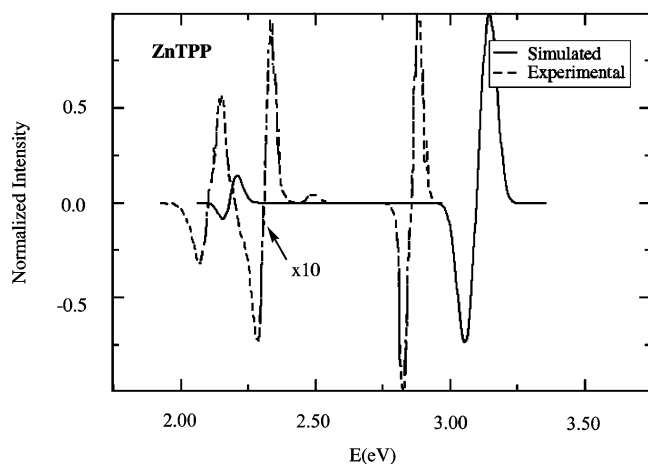


Figure 13. Experimental⁷⁷ and simulated MCD spectra of ZnTPP.

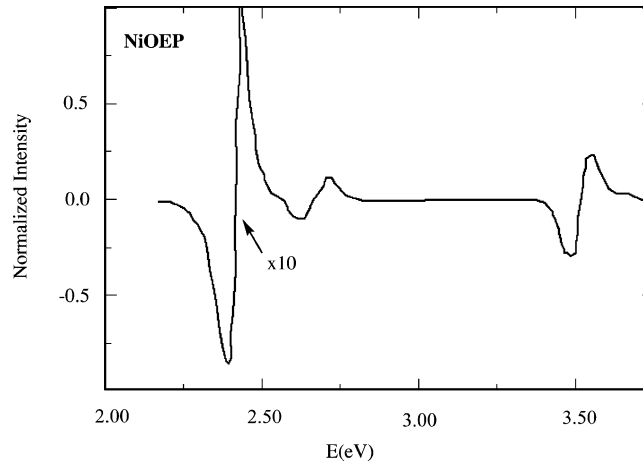


Figure 14. Experimental⁷⁰ MCD spectra of NiOEP.

hidden under the large positive \mathcal{A} term for $2E_u$. For nickel, we calculate in addition a ligand to metal charge-transfer transition corresponding to the $1e_u \rightarrow d_x^2 - y^2$ excitation at 3.16 eV. We do not count this transition in our numbering of the nE_u state for the sake of comparison with ZnTPP and MgTPP where it is absent. The $1e_u \rightarrow d_x^2 - y^2$ excitation has a modest absorption intensity ($f = 0.104$) with a small \mathcal{A} term ($\mathcal{A} = 0.02 \text{ D}^2$; $\mathcal{AD} = 0.09$) that is buried under the main $2E_u$ 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 $2E_u$ ($c_1 = -c_2$, Table 3). However, some mixture is observed with the one-electron

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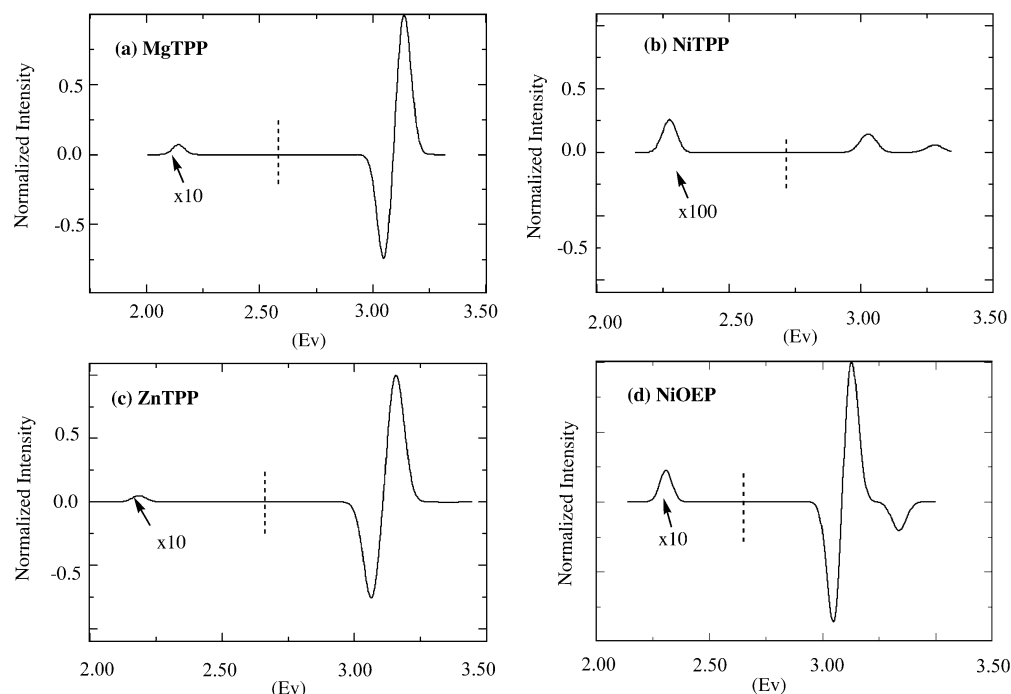


Figure 15. Simulated MCD spectrum of MTPP (M = Mg, Ni, Zn) and NiOEP based on \mathcal{B} terms alone.

Table 4. Calculated Transition Energies (eV), Oscillator Strength (f), \mathcal{A} , \mathcal{A}/\mathcal{D} , \mathcal{B} , and \mathcal{B}/\mathcal{D} Parameters for NiOEP

complex	symmetry	Exc. Energ.		composition	%	f	\mathcal{A}^c	\mathcal{A}/\mathcal{D}	\mathcal{B}^c	$\mathcal{B}/\mathcal{D}^c$	assign.	
		exp	calcd									
NiOEP	1E _u	2.25 ^a	2.31	1a _{1u} → 2e _g	57.97	0.034	1.07	5.25	42.89	2.11 × 10 ²	Q	
				2a _{2u} → 2e _g	40.79							
	2E _u		2.34	2e _u → d _{x²-y²}	94.42	0.000	1.11 × 10 ⁻⁵	0.44	0.07	2.94 × 10 ²		
				1e _u → d _{x²-y²}	4.77							
	3E _u	2.56		1b _{1u} → 2e _g	99.34	0.000	-4.11 × 10 ⁻⁴	-2.67	-0.66	-4.31 × 10 ³	B ^b	
		2A _{2u}	2.61		1b _{2u} → d _{x²-y²}	99.92	0.001	0.00	0.00	0.02		59.55
	4E _u		2.88 ^a	3.05	1b _{2u} → 2e _g	77.87	0.366	-3.37	-2.07	-2.03 × 10 ³		-1.24 × 10 ³
				1a _{1u} → 2e _g	11.15							
			3.12	2a _{2u} → 2e _g	8.89							
				2a _{2u} → 2e _g	42.26	0.920	-1.79	-0.45	2.34 × 10 ³	5.85 × 10 ²		
	5E _u			1a _{1u} → 2e _g	24.14							
	6E _u		3.34		1b _{2u} → 2e _g	19.4						
				1a _{2u} → 2e _g	92.65	0.130	1.27	2.40	-4.73 × 10 ³	-8.95 × 10 ²		
				d _{xy} , d _{xz} → 1b _{1u}	4.91							
				1e _u → 2e _g	12.74							
			1a _{1u} → 2e _g	23.58								

^a Ref 70. ^b B band = Soret band. ^c Atomic units.

excitation 1b_{2u} → 2e_g ($c_3 = 0.5$). In spite of this admixture, 2E_u for MgTPP and ZnTPP exhibits positive \mathcal{A}/\mathcal{D} and \mathcal{A} values similar to those obtained for 2E_u of NiTPP (Table 3). The second transition in the Soret band corresponds for NiTPP to the 3E_u state and it is primarily made up of the 1b_{2u} → 2e_g excitation with some admixture from the conjugated Gouterman state. The \mathcal{A}/\mathcal{D} term corresponding to 3E_u is negative for MgTPP (-2.17) and ZnTPP (-2.24) and very similar to NiTPP (-2.64) although slightly reduced numerically. However, the \mathcal{A} terms for MgTPP (-3.55 D²) and ZnTPP (-3.41 D²) are numerically much larger than for NiTPP (-0.18 D²). The reason for that is the larger f value for MgTPP (0.754) and ZnTPP (0.708) compared to that for NiTPP (0.034), as the result of the admixture of the conjugated Gouterman state into 3E_u. The experimental MCD spectrum of ZnTPP (Figure 13) exhibits,

as in the case of NiTPP (Figure 12), a positive \mathcal{A} band in the Soret region, which we might attribute to 2E_u. However, the experimental MCD spectrum does not reveal a second negative \mathcal{A} term for ZnTPP, as predicted computationally. We shall address this discrepancy in the next section, where we discuss the influence from the \mathcal{B} term on the MCD spectrum.

3.4.3. Influence of \mathcal{B} terms on the Simulated MCD Spectra of MTPP and NiOEP in the Q Region. It follows from our discussion of the MP systems that it is important to include the \mathcal{B} term into the simulation, to obtain good agreement with experiment. We shall thus discuss here the influence of the \mathcal{B} term on the simulated MCD spectra of the MTPP (M = Mg, Ni, Zn) and NiOEP systems. The expression for the \mathcal{B} term due to the coupling between

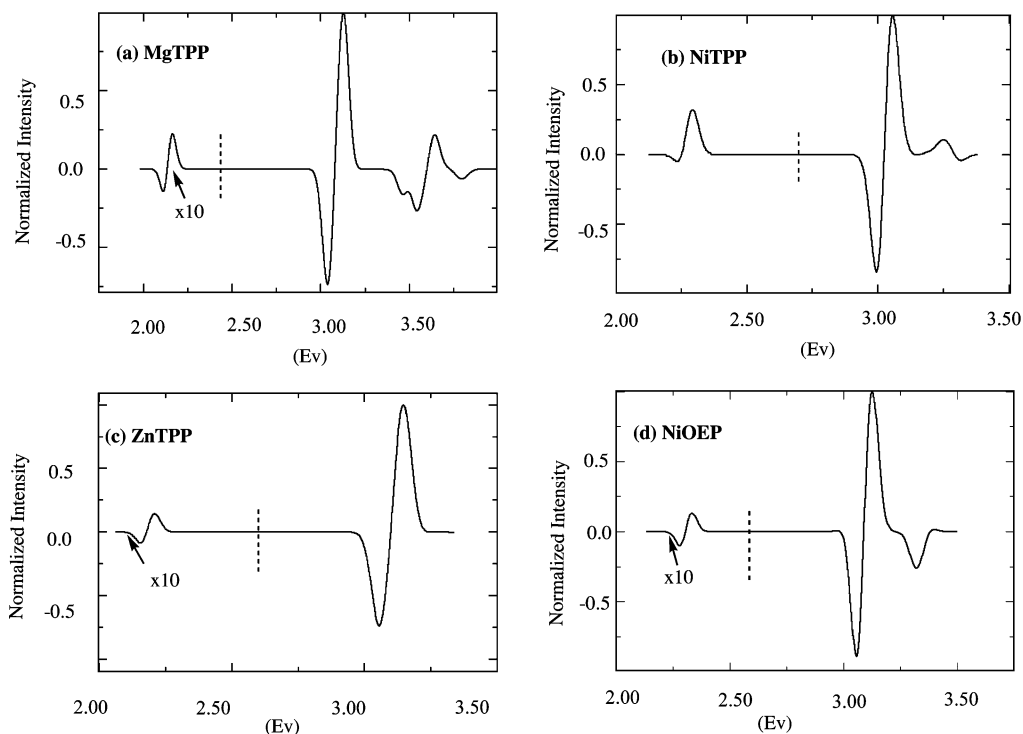


Figure 16. Simulated MCD spectrum of MTPP ($M = \text{Mg, Ni, Zn}$) and NiOEP based on \mathcal{A} and \mathcal{B} terms combined.

Table 5. Some of the Relevant Integrals Used to Calculate the \mathcal{AD} Term for the Q and B Bands of MTPP ($M = \text{Mg, Ni, Zn}$) and NiOEP

	ZnTPP	MgTPP	NiTPP	NiOEP
$\text{Im}\langle 2e_{gx} \hat{L}_z 2e_{gy} \rangle$	-2.758	-2.767	-2.490	-2.691
$\text{Im}\langle 1a_{1u} \hat{L}_z 2a_{2u} \rangle$	2.454	2.430	2.702	2.543

different excited states nE_u and pE_u by the magnetic field is given in eq 15.

As for the porphyrin complexes, the \mathcal{B} term in the Q-band region of MTPP ($M = \text{Mg, Ni, Zn}$) and NiOEP is small due to the large separation between the $1E_u$ state and other states of E_u symmetry (Figure 15). Thus, the Q-band region for the simulated MCD spectra of MTPP and NiOEP will be determined by the \mathcal{A} terms when \mathcal{A} and \mathcal{B} are combined (Figure 16). Indeed, the Q region in the experimental spectra is dominated by an \mathcal{A} term doubled by vibronic coupling (Figures 12–14).

3.4.4. Influence of \mathcal{B} Terms on the Simulated MCD Spectra of MTPP in the Soret Region. For NiTPP, we find only modest \mathcal{B} terms for $2E_u$ (3.03 eV) and $3E_u$ (3.28 eV) because the two states are relatively well separated (~ 0.25 eV, Figure 15). The simulated MCD spectrum for NiTPP is, as a consequence, dominated in the Soret region by a single positive \mathcal{A} term (Figure 16) in agreement with experiment (Figure 12).

The \mathcal{B} terms in the Soret region for $2E_u$ and $3E_u$ are much larger (and of opposite sign) in the case of MgTPP and ZnTPP compared to NiTPP because the energy separation between $2E_u$ and $3E_u$ is smaller for $M = \text{Mg, Zn}$ compared to $M = \text{Ni}$. The complex MCD spectra of MTPP ($M = \text{Mg, Zn}$) due to the \mathcal{A} term of one positive \mathcal{A} band followed by one negative \mathcal{A} band (Figure 11) is, as a consequence, overwritten by two \mathcal{B} terms of opposite sign (Figure 15) so that the total simulated MCD spectra appear to have a single

positive pseudo \mathcal{A} term (Figure 16) in agreement with experiment (Figure 12).

3.4.5. Influence of the \mathcal{A} and \mathcal{B} Term on the Simulated MCD Spectrum of NiOEP in the Soret Region. Turning finally to NiOEP, we find in the Soret region, two transitions 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 ($f = 0.920$, Table 4). The latter can be assigned to the intense transition observed at 3.22 eV. The $4E_u$ state is primarily represented by the $1b_{2u} \rightarrow 2e_g$ one-electron excitation, with some mixing from the conjugated Gouterman state $5E_u$, just as we have seen it for a number of MP and MTPP complexes. As in these cases, $4E_u$ exhibits a negative \mathcal{A} term and an intense negative \mathcal{B} term from the magnetic interaction with $5E_u$ (Figures 11 and 15). When \mathcal{A} and \mathcal{B} terms are combined, $4E_u$ is dominated by the negative \mathcal{B} term (Figure 16). The $5E_u$ state corresponds to the conjugated Gouterman state. It has a positive \mathcal{A} term and a positive \mathcal{B} term from the magnetic interaction with $4E_u$ (Figures 11 and 15). When the \mathcal{A} and \mathcal{B} terms are combined, $5E_u$ is dominated by the positive \mathcal{B} term (Figure 16). It is clear from the discussion that the simulated MCD spectrum in the Soret region is dominated by a negative \mathcal{B} term due to $4E_u$ followed by a positive \mathcal{B} term due to $5E_u$. The two \mathcal{B} terms have combined the appearance of a positive \mathcal{A} term in agreement with the experimental⁷⁰ MCD spectrum for NiOEP (Figure 14).

4. Concluding Remarks

We have presented a computational study on MCD exhibited by the porphyrin complexes MP ($M = \text{Mg, Ni, Zn}$), MTPP ($M = \text{Mg, Ni, Zn}$), and NiOEP where $P =$ porphyrin, TPP = tetraphenylporphyrin and OEP = octaethylporphyrin (Figure 2). The study makes use of a newly

implemented method⁴ for the calculation of \mathcal{A} and \mathcal{B} terms from the theory of MCD^{19–22} and is based on TD–DFT.^{56–59}

Following the qualitative work by Gouterman,⁴⁹ several studies,^{14,15,67,81,82} including the nearly quantitative DFT calculations by Baerends^{12,64} et al., have found that the Q band representing the absorption of lowest energy for the systems studied here is due to a single electronic transition from the A_g ground state to the degenerate $1E_u$ excited state (Tables 1, 3, and 4). The transition is in good agreement with experiment, calculated to take place in the energy region between 2.15 – 2.30 eV (depending on the system). The transition involves, in accordance with the four orbital model due to Gouterman,⁴⁹ the two degenerate virtual orbitals of $2e_g$ symmetry and the two nearly degenerate occupied orbitals of highest energy with a_{2u} and a_{1u} symmetry, respectively. The two one-electron excitations $2a_{2u} \rightarrow 2e_g$ and $1a_{1u} \rightarrow 2e_g$ contribute with about the same amplitude to the $1A_{1g} \rightarrow 1E_u$ transition (Tables 1, 3, and 4). Thus, the $1E_u$ state can, to a good approximation, be represented by a Gouterman state function $\Psi(gE_u)$ of the form given in eqs 10 and 11 where $c_1 = c_2 = 1/\sqrt{2}$ and $c_3 = c_4 = 0$.

It is well-known⁴⁹ that the Gouterman state function $\Psi(gE_u)$ gives rise to a low oscillatory strength because the two contributions to $\mathcal{D}(gE_u)$ from $1a_{1u} \rightarrow 2e_g$ and $2a_{2u} \rightarrow 2e_g$ nearly cancel. The cancellation results in a Q band of low intensity (Tables 1, 3, and 4). Our calculations reveal, on the other hand, that the contributions to

$$\mathcal{A}(gE_u^1)/\mathcal{D}(gE_u) \approx \mathcal{A}(1E_u)/\mathcal{D}(1E_u) \propto \text{Im}\langle 1E_{ux} | \hat{L}_z | 1E_{uy} \rangle \quad (16)$$

from $2a_{2u} \rightarrow 2e_g$ and $1a_{1u} \rightarrow 2e_g$ interfere constructively, giving rise to a positive \mathcal{A} term with large $\mathcal{A}\mathcal{D}$ values in the range of 5.5 to 5.0. However, the \mathcal{A} term parameter itself

$$\mathcal{A}(1E_u) \approx \text{Im}\langle (1E_{ux}) | \hat{L}_z | 1E_{uy} \rangle \mathcal{D}(gE_u) \quad (17)$$

is still modest because of the small oscillatory strength $\mathcal{D}(gE_u) \approx \mathcal{D}(1E_u)$ (Tables 1, 3, and 4). The corresponding \mathcal{B} term for the Q band was calculated to be positive and even smaller than the \mathcal{A} term. The small value for $\mathcal{B}(1E_u)$ can be understood from eq 15 when we note that the energy difference between the first excited-state and subsequent excited states [$W(1E_u) - W(pE_u)$] in the denominator is large ($\approx 10,000 \text{ cm}^{-1}$) compared to the magnetic terms in the numerator ($\approx 1 \text{ cm}^{-1}$) involving \hat{L}_z . When combined, the two terms appear as one positive \mathcal{A} term in the Q band region, in agreement with experimental findings.^{15,70,77,79,80}

The second (Soret) absorption band contains two excited states aE_u and bE_u of importance for the MCD spectrum in this region. They are $2E_u$ and $3E_u$, respectively, for MP(M

= Mg, Ni, Zn) and MTPP (M = Mg, Zn) (Tables 1, 3); $2E_u$ and $4E_u$, respectively, for NiTPP (Table 3) and $4E_u$ and $5E_u$, respectively, for NiOEP (Table 4). The corresponding transition energies are calculated in the range of 3 to 3.5 eV (depending on the system), in good agreement with experiment.

The Soret MCD spectrum can, in addition, be understood in terms of two approximate state functions $\Psi(g^*E_u)$ and $\Psi(hE_u)$. The first is the conjugated Gouterman state function of the form given in eqs 10 and 9 with $c_1 = -c_2 = 1/\sqrt{2}$ and $c_3 = c_4 = 0$. The second represents the one-electron excitation $b_{2u} \rightarrow 2e_g$ and is of the form given in eqs 10 and 11 with $c_3 = 1$ and $c_1 = c_2 = c_4 = 0$.

The conjugated Gouterman state function affords, in line with previous studies,⁴⁹ a large dipole strength as the contributions from $2a_{2u} \rightarrow 2e_g$ and $1a_{1u} \rightarrow 2e_g$ add up. We find on the other hand that $\mathcal{A}(g^*E_u)/\mathcal{D}(g^*E_u) \propto \text{Im}\langle g^*E_{ux} | \hat{L}_z | g^*E_{uy} \rangle$ is small (and positive) because the contributions from $2a_{2u} \rightarrow 2e_g$ and $1a_{1u} \rightarrow 2e_g$ interfere destructively. Finally, $\mathcal{A}(g^*E_u) \propto \text{Im}\langle g^*E_{ux} | \hat{L}_z | g^*E_{uy} \rangle \mathcal{D}(g^*E_u)$ is large (and positive) due to the sizable value of $\mathcal{D}(g^*E_u)$. On the other hand, $\Psi(hE_u)$ representing the one-electron excitation $1b_{2u} \rightarrow 2e_g$ affords minute (10^{-3} D^2) $\mathcal{D}(hE_u)$ and $\mathcal{A}(hE_u)$ parameters, whereas $\mathcal{A}(hE_u)/\mathcal{D}(hE_u)$ is negative (~ -1.5).

For NiP and NiTPP, the two states aE_u and bE_u are represented by $\Psi(g^*E_u)$ and $\Psi(hE_u)$, respectively. Thus, the MCD spectrum in the Soret region should exhibit a single positive \mathcal{A} term (Figures 6 and 11) that is in agreement with experiment (available for NiTPP only, Figure 12). Further, as a result of the relatively large separation between aE_u and bE_u of 0.2 eV, the size of the \mathcal{B} terms (Figures 8 and 15) as well as their impact on the MCD spectrum in the Soret region is modest (Figures 9 and 16).

For the remaining systems, aE_u and bE_u are close in energy ($< 0.05 \text{ eV}$), with each of the states represented by a majority part from one of the approximate functions $\Psi(g^*E_u)$ and $\Psi(hE_u)$ as well as a minority of the other (Tables 1, 3, and 4). On the basis of the \mathcal{A} terms alone, aE_u and bE_u exhibit a MCD pattern of one positive and one negative \mathcal{A} term (Figures 6 and 11), in disagreement with the recorded MCD spectra of ZnP (Figure 5), ZnTPP (Figure 13), and NiOEP (Figure 14). However, the close proximity of the two states makes for two large \mathcal{B} terms (Figures 8 and 15) as the denominator in eq 15 becomes small. The two \mathcal{B} terms of the negative (lower energy) and positive sign (higher energy) dominate the simulated MCD spectra (Figures 9 and 16, respectively) and give the appearance of a single positive \mathcal{A} term in agreement with experiment. That the two \mathcal{B} terms are of opposite signs is readily deduced from eq 15 if we only take the magnetic coupling between aE_u and bE_u into account and neglect contributions from all other excited states.

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