Transition Assignments in the Ultraviolet−Visible Absorption and Magnetic Circular Dichroism Spectra of Phthalocyanines

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In a recent paper, Mussleman and co-workers[1] (we refer to this paper as HFFM throughout) proposed a revised band assignment scheme for the optical spectra of D_{4h} metal phthalocyanine complexes (M(II)Pc(−2)), known systematically as tetraazatetrabenzporphyrins, based on an analysis of a polarized specular reflectance spectrum of a D_{2h} model complex, Fe(β-dtpy)$_2$.4THF, and comparison with theoretical calculations reported previously.[2] Finally, HFFM use spectral data obtained from an earlier study of partially oxidized (I)CuPc single crystals (iodine was present as an axial ligand) to provide support for this proposal.[3] HFFM state that that their data are inconsistent with Gouterman's four-orbital LCAO model,[4] which along with its later modifications[5] has been used very widely and successfully to describe the optical spectra of both metal porphyrin and metal phthalocyanine complexes over the past 4 decades.[4−6] Because the proposed band assignment scheme put forward by HFFM would radically change the basis for spectral analysis of a very wide range of compounds and could lead to considerable confusion, we feel it appropriate to carefully reconsider the spectroscopic and theoretical evidence for Gouterman's four-orbital model.

The four-orbital model is based on a theoretical treatment that unites a cyclic polyene model[4,7] with a Huckel calculation[5] that takes into account the structure of the porphyrin or phthalocyanine ring. The orbital angular momentum (OAM) associated with pairs of orbitals in the inner perimeter 16 atom, 18 π-electron aromatic ring system follows from the assignment of the molecular orbitals of a cyclic polyene aromatic ring in terms of wave functions in an ascending energy sequence where $M_L = 0, \pm1, \pm2, ..., \pm7, 8$. The HOMO has an M_L value of ±4, while the LUMO has an M_L value of ±5. In this relatively simple scheme, there are four possible transitions between these two levels involving changes in orbital angular momentum (ΔM_L) of ±1 and ±9. The allowed (±1) and forbidden (±9) nature of the B and Q bands, respectively, of metal porphyrin (MP) complexes is reflected in the significantly different molar extinction coefficients. ΔM_L values can be derived experimentally from the A_1/D_0 MCD parameter, which is proportional to the OAM difference between the ground and excited states.[4,6,7c,d] The observed A_1/D_0 values were found to be in close agreement with those predicted by Gouterman's calculations. Despite the obvious simplicity of Gouterman's model, it provides a remarkably good description of the experimental spectral data of main group MP(−2) and MPc(−2) complexes.[4]

In the case of MP(−2) complexes, Gouterman's MO calculations[5] have indicated that the a_{1u} and a_{2u} HOMOs are accidently degenerate but the Q (or α) band at ca. 600 nm and the B (or Soret) band at ca. 420 nm retain their respective forbidden and allowed character. In the case of MPc(−2) complexes, Gouterman proposed that the aza linkages and fused benzenes break the accidental degeneracy of the a_{1u} and a_{2u} orbitals significantly, resulting in less mixing between the two excited states such that the previously forbidden Q transition gains significant intensity; the Q band is actually observed as an intense band with a molar extinction coefficient of about 10^5 near 670 nm.[6b] The A_1/D_0 ratios obtained from moments analysis of the ZnPc(−2) Q spectral regions of the MCD and UV−visible absorption data are greater than 3.0, indicating that there is still considerable configuration interaction (CI) between the Q and B excited states and that the Q band retains some of its forbidden character.[6] A minor degree of CI between these states has also been predicted by more recent ZINDO calculations of MPc(−2).[8]

We have used Gouterman's model as the theoretical framework within which to assign the bands observed in the optical spectra of a variety of MP(−2) and MPc(−2) complexes, as well as their cation and anion radical species, in all cases basing our assignment (see Figure 1) on spectral deconvolution studies of the UV−visible absorption and MCD spectroscopy[6,9] using the SIMPFIT program.[10] Our spectral deconvolution studies[6b] have indicated that there are in fact two A terms in the B region of the spectrum that we believe arise primarily as a result of CI between the $1a_{2u} \rightarrow 1e_g^*$ B transition ($1a_{2u} \rightarrow 1e_g^*$) from the four-orbital model and a $1b_{1u} \rightarrow 1e_g^*$ one-electron transition.[8] Gouterman's band nomenclature system was, therefore, modified many years ago to include separate B1 and B2 transitions.[6b] Analysis of MCD spectra of a number of MPc(−2) compounds

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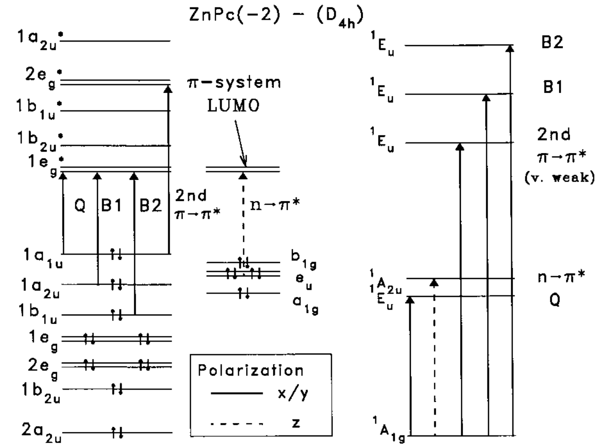

Figure 1. Molecular orbital and state level diagrams of ZnPc(−2) showing the transitions that are predicted to give rise to absorption bands in the 300−1000 nm range. Analysis of the MCD spectra observed for MPc(−2) complexes has identified seven separate A terms in the 250−800 nm region arising from transitions to doubly degenerate excited states. The associated bands are referred to in the sequence Q, 2nd $\pi \rightarrow \pi^*$, B1, B2, N, L, and C in ascending energy and have been identified through spectral deconvolution studies[6,8a] on the basis of Gouterman's model.[5b] A recent ZINDO calculation of the absorption spectrum of ZnPc(−2) predicted the presence of a much weaker 2nd $\pi \rightarrow \pi^*$ transition ($1a_{1u} \rightarrow 2e_g{}^*$), which had not previously been associated with an identifying letter.[8a] An n $\rightarrow \pi^*$ transition is placed between the Q and B1 transitions in energy on the basis of a spectral deconvolution analysis of the absorption and MCD spectra of (CN)-ZnPc(−2)[9b] recorded at cryogenic temperatures. The orbital ordering on the left is based on the results of the ZINDO calculation.

and ZINDO calculations has subsequently resulted in the identification of a very weak band slightly to the red of the B1 band that is believed to arise from a 2nd $\pi \rightarrow \pi^*$ transition into the $2e_g{}^*$ orbital of MPc(−2) [8a] (Figure 1).

We turn now to the evidence offered in the paper by HFFM[1] to support their proposal that Gouterman's band assignment scheme should be changed. In their work, they analyze the spectral reflectance data of their D_{2h} symmetry model compound and use their conclusions to interpret the solid-state optical data reported previously[3] for a partially oxidized CuPc species. They identify a weak band at 555 nm to the blue of the main Q band at 660 nm as a second $\pi \rightarrow \pi^*$ band. HFFM state that this band is associated with the $a_{2u} \rightarrow e_g{}^*$ transition (the B transition in Gouterman's four-orbital scheme), basing their proposal on the results of an MO calculation reported in a previous paper by Musselman and co-workers.[2] HFFM[1] refer to this peak as the R band and state that the observed intensity in the B (or Soret) region is due to an $e_g \rightarrow b_{2u}{}^*$ transition, which was not included in Gouterman's assignment scheme. No comparison data are provided with the exception of a table aligning the original Gouterman four-orbital assignments with their new proposed assignment scheme. HFFM state that the much larger ΔHOMO in the case of MPc(−2) molecules completely eliminates the CI between the Q and B excited states and that this leads to a complete lifting of the forbidden nature of the Q band. The authors make no reference to any of the available MCD spectral data[6,9] or to more recent ZINDO MO calculations that have been reported for a range of MPc(−2) complexes,[8] which provide no support for this conclusion.

HFFM[1] claim that Gouterman assigned the entire Q spectral envelope (500−720 nm) and the entire Soret region (250−400 nm) to electronic and vibrational bands arising from only the Q and B transitions, respectively. The authors state that there is an alternative interpretation for these regions according to calculations reported by Henriksson et al.[11] who are said to have predicted multiple electronic transitions for both the Q and Soret regions. It should be noted that both of these models were, in fact, based on five major $\pi \rightarrow \pi^*$ bands referred to as Q, B, N, L, and C in terms of ascending energy (the B1/B2 assignment postdated the theoretical work) and that the calculated energies and assignments for these bands in both calculations are very similar. The major point of disagreement between the models of Gouterman[5d] and Henriksson et al.[11] was related to the energy of the n $\rightarrow \pi^*$ bands associated with the aza nitrogen lone pair orbitals of the phthalocyanine ring. Gouterman and co-workers[5d] calculated that the lowest $n\pi^*$ excited state had an energy similar to that of the Q transition. They postulated that significant band broadening observed in the Soret region of MPc(−2) spectra relative to analogous MP(−2) complexes was due to the presence of underlying $n\pi^*$ excited states and pointed to the fact that Hochstrasser and Marzzacco[12] observed this broadening effect empirically in a study of the optical spectra of a variety of aromatic and heteroaromatic molecules. In contrast, Henriksson et al.[11] proposed that the n $\rightarrow \pi^*$ bands sit within the B (or Soret) region spectral envelope. It was Gouterman rather than Henriksson et al.,[11] therefore, who proposed that there could be multiple spin-allowed electronic transitions in the Q spectral region. Significantly and in contrast with the paper of HFFM,[1] neither model contained multiple spin-allowed $\pi \rightarrow \pi^*$ bands in the Q region. Henricksson et al.[11] predicted the presence of a number of triplet excited states at energies similar to that of the Q transition, but these are spin-forbidden and are not relevant in terms of the electronic absorption spectrum.

The nature of the spectral envelope in the Q region has since been extensively studied by different optical spectroscopic techniques at high resolution and over a wide range of temperature.[6b,9] In HFFM's[1] proposed assignment scheme, two separate $\pi \rightarrow \pi^*$ transitions are said to give rise to bands in the Q spectral region. Since both these transitions involve doubly degenerate excited states, this should result in a pair of intense *xy* polarized derivative-shaped A terms in the MCD spectrum.[13] Our recent spectral deconvolution analysis of the UV−visible and MCD spectra of ZnPc(−2) Q spectral region[9b] recorded at cryogenic temperatures indicates that the bands to the blue of the main Q_{00} at 670 nm are all Gaussian shaped B terms. The energies of the vibrational bands identified by spectral deconvolution were in good agreement with those reported in the Shpol'skii matrix emission studies of Huang et al.[14] These authors proposed that there is a *z*-polarized transition at 604 nm that gives rise to a second set of weak vibrational bands to

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(13) The MCD signal arises from the same transitions as those seen in the UV−visible absorption spectrum, but the selection rules are different because the intensity mechanism depends on the magnetic dipole moment in addition to the electric dipole moment, which normally determines UV−visible absorption intensity.[17] MCD spectroscopy is, therefore, complementary to UV−visible absorption spectroscopy because it can provide ground and excited state degeneracy information essential in understanding the electronic structure of molecules of high symmetry. The specificity of the MCD technique arises from three highly characteristic spectral features, the Faraday A, B, and C terms.[17] The derivative-shaped Faraday A term is temperature-independent and identifies degenerate excited states, while the normally Gaussian shaped C term is highly temperature-dependent and identifies an orbitally degenerate ground state. Gaussian shaped, temperature-independent B terms arise from mixing between closely related states linked by a magnetic dipole transition moment.

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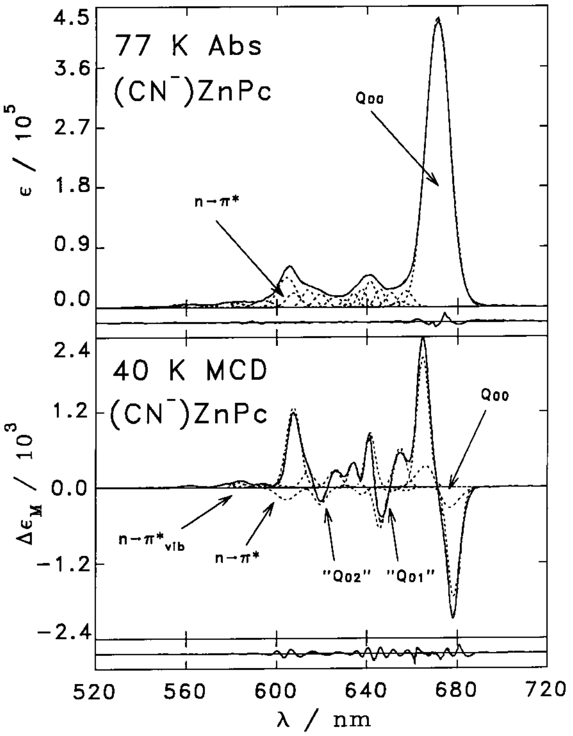

Figure 2. Spectral deconvolution analysis of the Q spectral region ZnPc(CN). The same bandwidths and centers are used to fit MCD and UV−visible absorption spectra recorded at cryogenic temperatures on the same 5:2 dimethylformamide/dimethylacetamide vitrified solution.

the blue of the Q transition because the fluorescence excitation and emission spectra deviated significantly from the anticipated mirror image pattern. Our deconvolution analysis[9b] (Figure 2) identified four intense B terms in a +/−/+/+ pattern in order of ascending energy labeled "Q_{01}", which is followed by a second set of +/−/+/+ bands 700 cm^{-1} to the blue labeled "Q_{02}". Huang et al.[14] proposed that this second repeating set of Q_{vib} bands are overtones of the first sequence that arise from a second quantum of vibrational energy from a totally symmetric a_{1g} vibrational mode. At the high-energy edge of the "Q_{02}" sequence there is a marked difference in the energies of the main absorption and MCD intensity at ca. 600 nm at the energy of Huang et al.'s proposed n → π* band. The bands to the blue of the negative B term at 604 nm are all positive B terms and are significantly broader than the Q_{vib} bands to the red. Under D_{4h} symmetry this is the pattern that would be expected for bands arising from the *z*-polarized n → π* transition out of the aza nitrogen lone pair orbitals proposed by Huang et al.[14]

Michl[6c,d] has demonstrated that even when the symmetry is reduced below D_{4h} the derivative-shaped *xy*-polarized A terms are replaced by intense coupled pairs of oppositely signed *x*- and *y*-polarized Gaussian shaped B terms. No second pair of intense coupled B terms has been observed in the MCD spectra of D_{2h} complexes of phthalocyanines at the wavelength predicted for HFFM's R transition.[1] The authors do not make it entirely clear whether the partially oxidized CuPc species[3] that is referred to is a neutral complex or a cation radical. If it is a cation radical species, then their R transition could correspond to an intense broad B term at around 510 nm that is a characteristic feature observed within the MCD spectra of $[MPc(-1)]^+$ species.[6c,d,8a,9b] We have recently assigned this band to a *z*-polarized n → π* transition due to the apparent nondegenerate excited state.[8a] Other authors[15] have proposed, on the basis of MO calculations, that this band is due to an *xy*-polarized π → π transition into the partially filled HOMO. Neither of these proposals appears to have been taken into account the papers by Musselman and co-workers.[1−3]

HFFM[1] state that the D_{2h} symmetry of their model compound allows them to observe spectral features hitherto unavailable in the case of D_{4h} complexes. It should be noted that MCD spectroscopy readily provides significantly more information for complexes of all symmetries than can be obtained from solid-state polarized specular reflectance spectra. Data are obtained at dramatically greater signal to noise ratios providing information about ground and excited-state degeneracies and band polarizations. Since MCD spectra can be recorded in solution, there are far fewer experimental problems associated with the technique, such as the Davydov splitting effects and the difficulty in obtaining accurate intensities via Kramers−Kronig transformation, which greatly complicate the analysis of specular relectance spectra. The authors have omitted the extensive literature that exists on the MCD spectroscopy of both D_{4h} and lower symmetry MP(−2) and MPc(−2) complexes from a number of different research groups.[6,8a,9,16]

In summary, we propose that the four-orbital model of Gouterman should continue to form the basis of the assignments of the optical spectra of both D_{4h} and lower symmetry MP(−2) and MPc(−2) complexes. The spectral deconvolution analyses of MCD spectral data for the Q spectral envelope of ZnPc(−2)[9b] shown in Figure 2 provides definitive evidence that there is no second, allowed π → π* band in the Q spectral region arising from the $1a_{2u} \rightarrow 1e_g^*$ transition. There is instead a weak n → π* band associated with the aza nitrogen lone pairs, as Huang et al.[14] and Gouterman and co-workers[5d] have previously predicted.

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