Chapter 3

ELECTRONIC STRUCTURES AND ABSORPTION SPECTRA

Gouterman Four-Orbital Model

Martin Gouterman first proposed the four-orbital model in the 1960s to explain the absorption spectra of porphyrins [17, 18]. According to this theory, the absorption bands in porphyrin systems arise from transitions between two HOMOs and two LUMOs, and it is the identities of the metal center and the substituents on the ring that affect the relative energies of these transitions. The HOMOs were calculated to be an a_{1u} and an a_{2u} orbital, while the LUMOs were calculated to be a degenerate set of e_g orbitals (see figure 3.1). Transitions between these orbitals gave rise to two excited states, both of ^1E_u character. Orbital mixing splits these two states in energy, creating a higher energy ^1E_u state with greater oscillator strength, giving rise to the Soret band, and a lower energy ^1E_u state with less oscillator strength, giving rise to the Q-bands.

Corrole Four-Orbital Model

Work first by Hush and co-workers[19], and later more quantitatively by Ghosh and co-workers[20], has shown that this four-orbital model also holds for corrole systems. However, the quantitative treatment is not necessary for a basic understanding of the corrole four-orbital model. Instead, a qualitative understanding can be achieved by considering what happens to the porphyrin orbitals when the corrole C_{2v} symmetry is

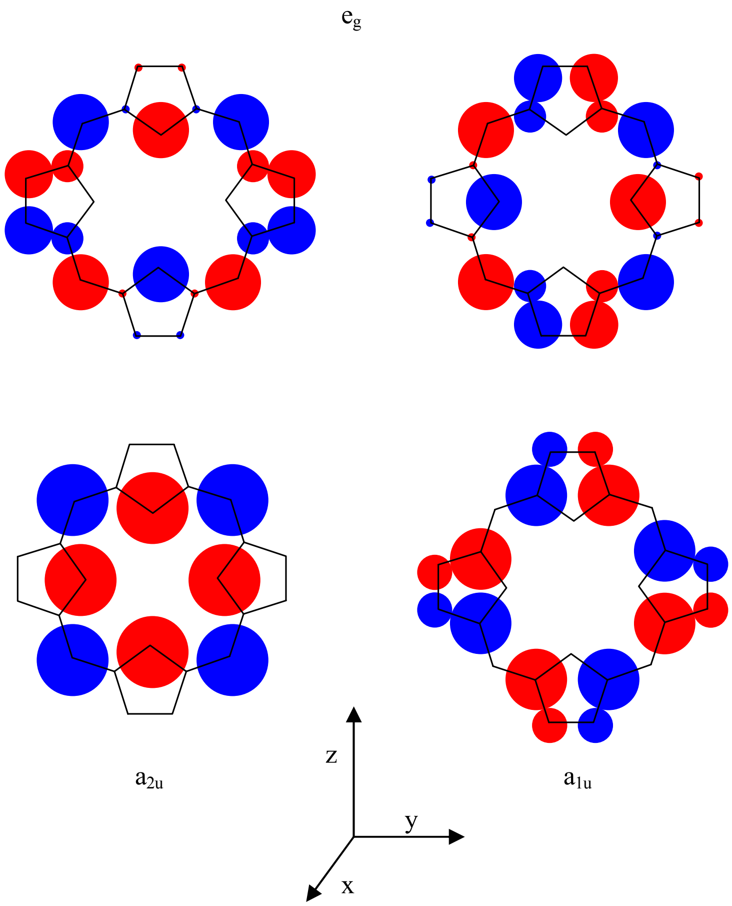

Figure 3.1. Porphyrin HOMOs (bottom row) and LUMOs (top row) (as shown in reference 17). In the corrole C_{2v} symmetry, the e_g orbitals transform as an a_2 and a b_1; the a_{2u} transforms as a b_1; the a_{1u} transforms as an a_2 orbital.

imposed. The a_{1u} and a_{2u} porphyrin HOMOs become a_2 and b_1, respectively, and the e_g LUMOs split into another set of a_2 and b_1 orbitals. Transitions between these give rise to four excited states, two $^1A_1$ and two $^1B_2$ (see figure 3.2). Again, orbital mixing will split the relative energies of these states as shown in figure 3.2. This mixing will affect the relative oscillator strength of the states as with porphyrins, and the relative intensities of the bands remains unchanged, the Q-bands are still much weaker than the Soret (see table 3.1). As well, the Soret band of corroles would now be expected to split, unless the transitions to these states are accidentally degenerate. However, in the cases of the corroles studied here, the metal complexes show no splitting of the Soret band (not to be confused with the vibronic shoulder seen on this band for the metallocorroles). **1** does show a wider Soret band than in the metallocorrole cases, indicating some unresolved splitting, and in **2** the splitting is observed, though the peaks are not resolved to baseline (see figures 3.3-3.5).

In Ghosh's calculations, he showed that an unsubstituted gallium corrole (that is, with only hydrogens at the eight β and three meso positions) had two nearly degenerate HOMOs and two nearly degenerate LUMOs, and that these frontier orbitals were "well-separated energetically from the rest of the orbital energy spectrum."[20] As well, his calculations showed that the HOMOs and LUMOs both did indeed consist of one a_2 and one b_1 orbital. In considering the relative energies for the two HOMOs, a crude approximation can be made by comparison to the a_{1u} and a_{2u} HOMOs of a metalloporphyrin. As stated above, theoretical desymmetrization of these orbitals transforms them to a_2 and b_1, respectively. Thus, like the a_{1u} porphyrin orbital, the a_2 corrole orbital has very little to no amplitude at the meso positions, while the b_1 has large amplitude at these positions, as does the a_{2u} in the

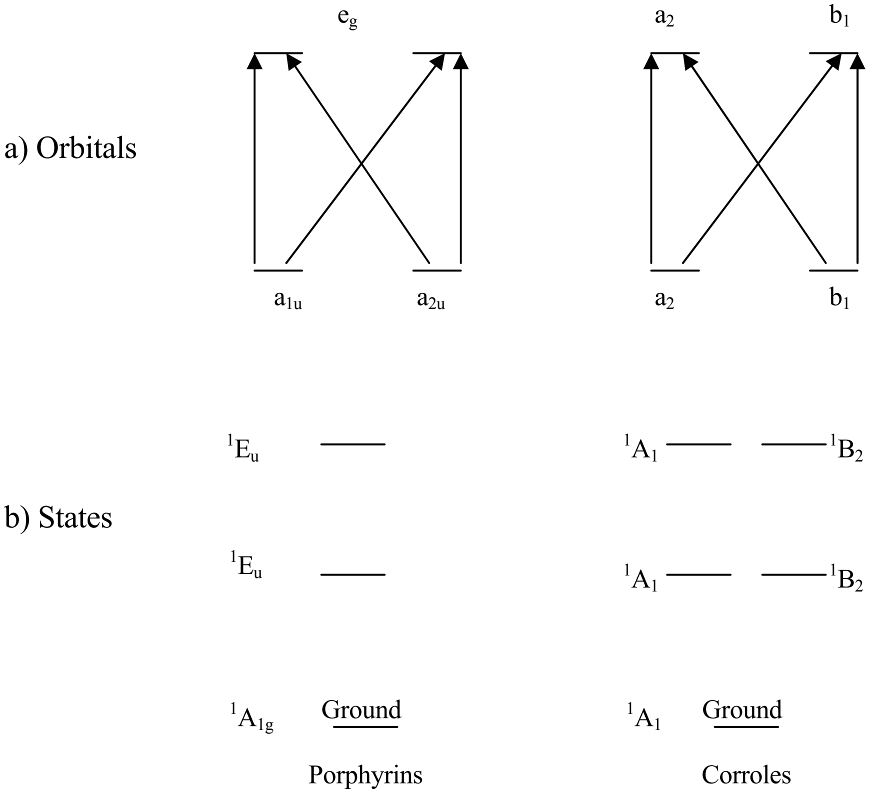

Figure 3.2. a) Orbital diagrams showing possible transitions for porphyrins and corroles. Note that while the HOMOs are shown to be degenerate in both cases, the actual relative energies will depend on the substitution of the rings. b) State diagrams showing possible excited states for porphyrins and corroles. Relative energies for the porphyrin case are taken from reference 17. In the absence of quantitative data for the corrole case, the states are shown as two sets of accidentally degenerate states.

Compound	Soret bands λ [nm] (ε x 10^{-3} [M^{-1}*cm^{-1}])	Q-bands λ [nm] (ε x 10^{-3} [M^{-1}*cm^{-1}])
1 (CH_2Cl_2)	408 (114.0)	560 (17.6), 602 (9.3)
2 (pH 7.0 buffer)	414 (71.0), 430 (62.0)	588 (15.0), 620 (27.0)
1-Ga (CH_2Cl_2)	398 (57.3), 420 (284)	568 (17.1), 594 (23.6)
2-Ga (pH 7.3 buffer)	424 (75.0)	588 (13.6), 610 (17.3)
1-Sn (CH_2Cl_2)	396 (47.0), 416 (215)	566 (15.0), 588 (14.0)
2-Sn (MeOH)	424 (140)	582 (16.0), 602 (18.0)

Table 3.1. Absorption peaks and epsilons for the 6 closed shell corroles.

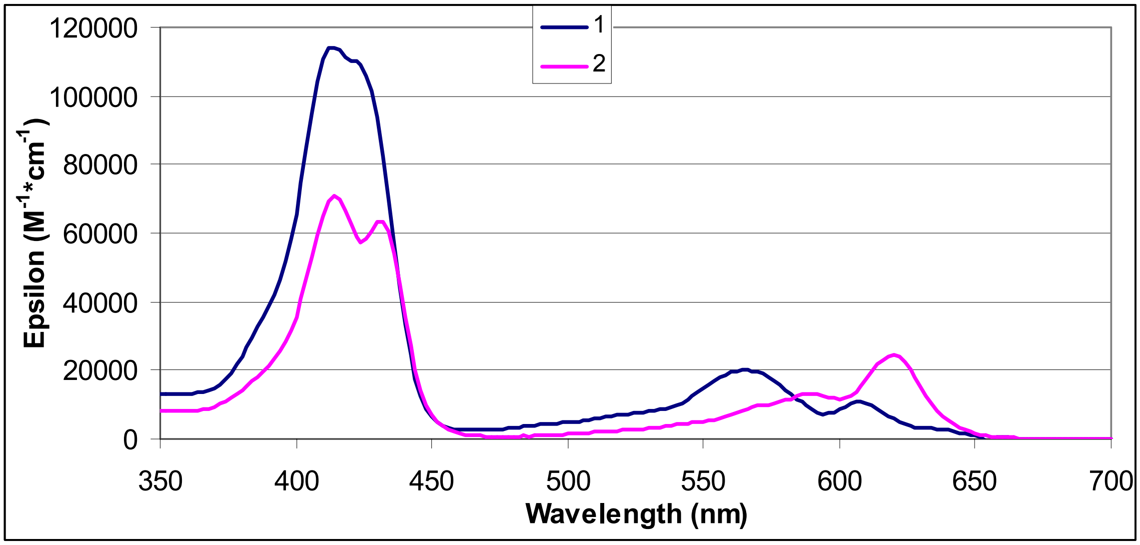

Figure 3.3. Absorption spectra of **1** (blue) and **2** (pink).

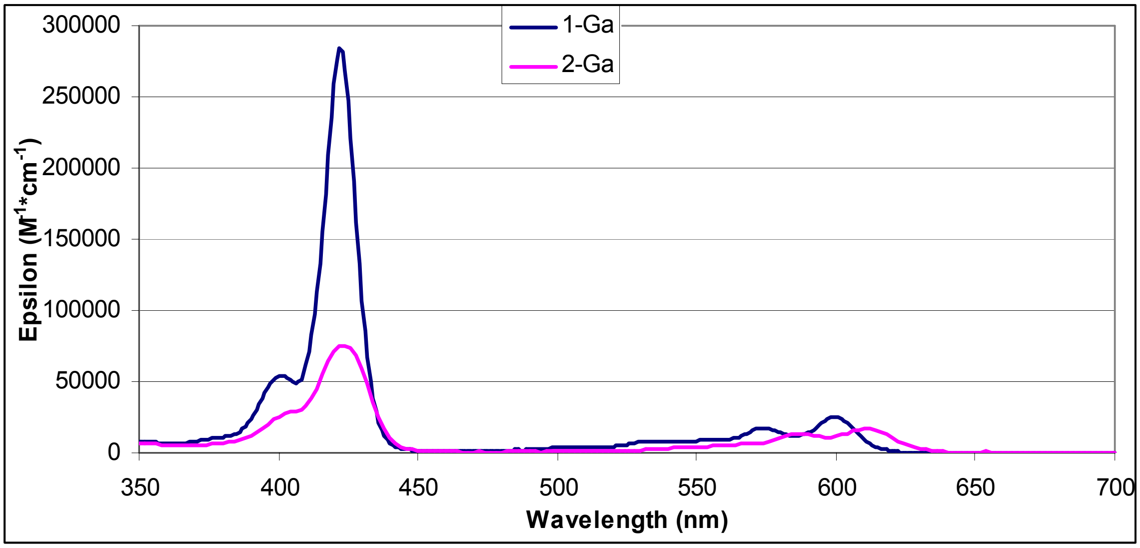

Figure 3.4. Absorption spectra of **1-Ga** (blue) and **2-Ga** (pink).

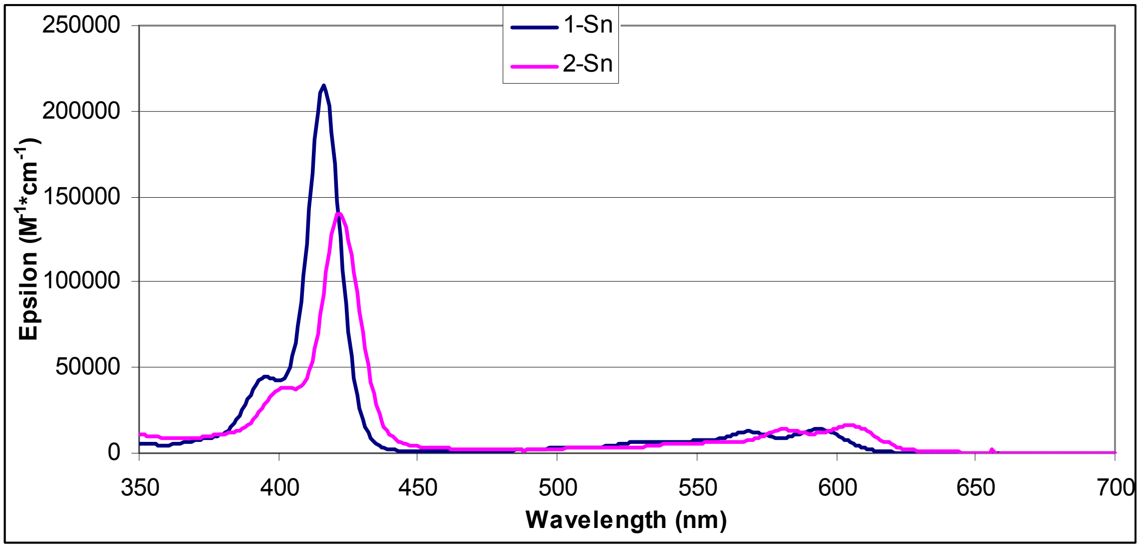

Figure 3.5. Absorption spectra of **1-Sn** (blue) and **2-Sn** (pink).

porphyrin case. Therefore, in the cases of the corroles used in this study, with very electron withdrawing pentafluorophenyl groups in the meso positions, the b_1 orbital should be stabilized (lowered in energy), making the a_2 orbital the higher of the two HOMOs when the degeneracy is broken. However, it has been shown with porphyrins that the main effect of a metal in the system is conjugation of its p_π orbital with the π electrons of the ring, and because of the nodal properties of the HOMOs, the metal can only interact with the a_{2u} orbital[17], or the b_1 corrole orbital. A more electropositive metal will raise the energy of this orbital and can be evidenced by a red-shifting of the visible bands of the spectrum. Therefore the relative energies of the two HOMOs in a porphyrin or corrole will depend on the combination of these two factors.

These assumptions can be shown to hold by consideration of the absorption spectra of the free-bases, gallium, and tin complexes used in this study. Consider first the gallium versus tin species. In both the sulfonated and non-sulfonated cases, the bands of the gallium corrole are red-shifted with respect to those of the tin corroles. The ionization potential of the gallium(III) ion is 64 eV, and the ionization potential of tin(IV) is 72.28 eV[21]. Thus, gallium(III) has a lower electron affinity and is expected to be more electropositive, and the red-shift of the absorption bands is as expected.

The effect of β substituents on the corrole ring is harder to predict qualitatively. However, if the HOMOs and LUMOs of the corrole do resemble their porphyrin counterparts, the b_1 HOMO should have little to no electron density on the β carbons, the a_2 HOMO should have electron density clouds with large lobes on the α carbons and smaller lobes on the β carbons, and the LUMOs should have clouds with small lobes on the α carbons and large lobes on the β carbons. Thus a β substituent should not interact with the b_1 orbital, but should have some interaction with the a_2 orbital, and a larger interaction with the LUMOs. Therefore, to a first approximation, an electron withdrawing group, such as the sulfonyl groups used here, would be expected to stabilize the LUMOs more than the HOMOs, lowering the gap and producing an overall red-shift in the spectrum. The fact that this is indeed what is observed when comparing each non-sulfonated corrole to its sulfonated counterpart would give some credence to this theory. However, care must be taken in ascribing the absorption shifts to this effect. The relative energetics with regard to the β substituents on a corrole are delicately balanced, and the specific mechanisms producing the shifts are not fully understood.

Conclusions

Comparisons between corrole spectra and porphyrin spectra would seem to indicate that the Gouterman four-orbital model widely used to explain porphyrin absorption should be valid for corrole absorption as well. By imposing the symmetry restrictions of a corrole on the frontier orbitals of porphyrins, the model can be adapted for corroles, and it is seen that it does indeed describe the electronic spectra very well. Even under the reduced symmetry of corroles, the transitions between excited states show the same mixing effects as porphyrins, providing relatively high intensity Soret bands at lower wavelengths, and relatively low intensity Q-bands at higher wavelengths. Interestingly, while the Soret bands are no longer required to be degenerate, only the free-base complexes show any evidence of splitting of these bands.

As well, by applying the corrole symmetry to the porphyrin orbitals, correlations can be made regarding the electronic nature of the corrole HOMOs and LUMOs, allowing first order predictions as to the effects of meso and β substituents, and the effect of the metal ion in metallocorroles. These predicted effects can be seen in the absorption spectra of the corroles, further validating the use of the four-orbital model for these systems.