Orbital Ordering in β-Substituted Porphyrins: Resonance Raman Spectra of the Radical Cations

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Introduction

There is much interest in the effects of different peripheral substituents on the electronic structure of the porphyrin ring, particularly on the ordering of the two highest occupied orbitals a_{1u} and a_{2u}, which has a significant influence on the structure and reactivity of porphyrin π-cation radicals.[1] Because these orbitals have different nodal patterns (Figure 1),[2,3a] the positions of substitution are as important as the electronic properties of the substituents. Thus, donor groups at the pyrrole β positions raise the energy of the a_{1u} orbital because its electron density is concentrated on the pyrrole rings, while donor groups at the methine bridges raise the energy of the a_{2u} orbital because its electron density is concentrated on the C_m (as well as the N) atoms.[2] It is known that *meso*-tetraphenylporphyrins (TPP) produce cation radicals with a_{2u} character, while octa-β-alkyl porphyrins produce cations with a_{1u} character.[3] Recently, Binstead et al.[4] investigated a series of TPP's with single β substituents (TPP-β, Figure 1) and evaluated the relative energies of the HOMOs in the neutral Cu complexes, using a combination of redox potentials and electronic transition energies. The analysis indicated a reversal of a_{2u}/a_{1u} ordering when electron-withdrawing groups (e.g. $-NO_2$ and $-CHO$) are replaced by electron-donating groups (e.g., $-OCH_3$ and $-NH_2$). This is the first test of orbital switching with a graded series of single substituents on otherwise identical porphyrins.

We thought it worth examining the cation radicals, using resonance Raman (RR) spectroscopy, since marker bands of orbital character have been identified.[3]

Experimental Section

Synthesis. Preparation of the β-substituted CuTPP's (CuTPP-β, Figure 1) are described by Binstead et al.[4] and in the literature.[5] C_β-deuterium-labeled (d_7) CuTPP-CHO was made by refluxing CuTPP-d_8 (0.084 g) with DMF (0.7 mL) and phosphonyl chloride (0.7 mL) in 1,2-dichloroethane (11 mL).[6] The product was extracted with chloroform, washed three times in water, and dried with Na_2SO_4, and the solvent was evaporated under vacuum. The porphyrin was recrystallized in 1:5 CH_2Cl_2/CH_3OH. Absorption spectra, obtained in CH_2Cl_2 with an HP 8452A UV/vis spectrometer, agreed with published spectra of the neutral CuTPP-β molecules.[4]

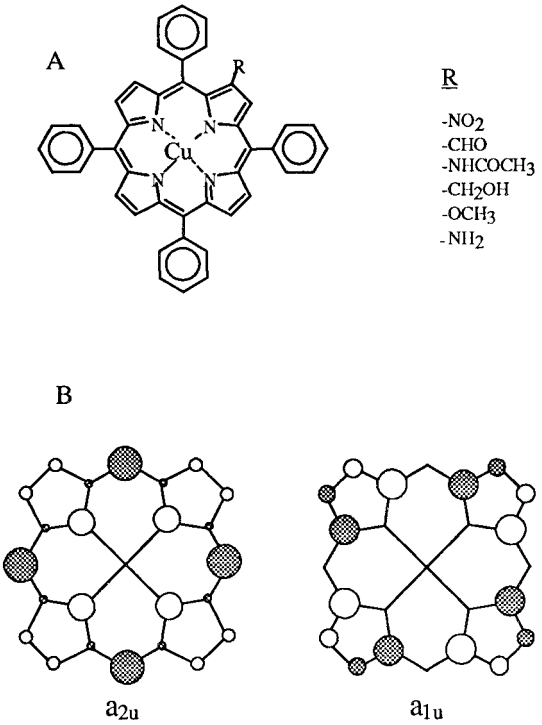

Figure 1. (A) Schematic representation of the copper 2-substituted tetraphenylporphyrins (MTPP-β). R = 2-substituent. (B) Schematic representation of the metalloporphyrin highest occupied molecular orbitals, a_{1u} and a_{2u}. The sizes of the circles are proportional to the atomic orbital (AO) coefficients of magnesium porphine. The black and white circles represent positive and negative signs, respectively, of the upper lobes of the p_π orbitals.[2,3]

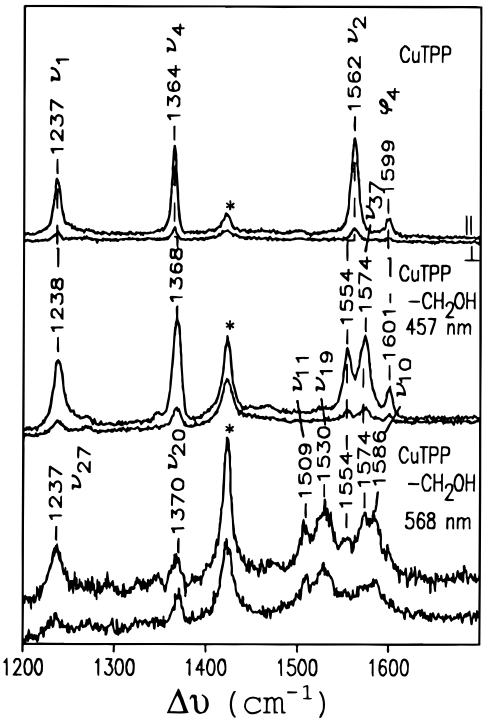

Figure 2. RR spectra of CuTPP (top spectra) in CH_2Cl_2/0.1 M TBAP obtained with 457.9 nm excitation, CuTPP-CH_2OH (middle spectra) in CH_2Cl_2/0.1 M TBAP obtained with 457.9 nm excitation, and CuTPP-CH_2OH (bottom spectra) in CH_2Cl_2 obtained with 568 nm excitation. Parallel (∥) and perpendicular (⊥) polarizations are shown. Asterisks (*) mark a solvent band.

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(1) (a) Barkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1988**, *110*, 7566. (b) Gudowska-Nowak, E.; Newton, M. D.; Fajer, J. *J. Phys. Chem.* **1990**, *94*, 5795.
(2) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1−165.
(3) (a) Czernuszewicz, R. S.; Macor, K. A.; Li, X.-Y.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 3860−3869. (b) Oertling, W. A.; Salehi, A.; Chang, C. K.; Babcock, G. T. *J. Phys. Chem.* **1989**, *93*, 1311−1319.
(4) Binstead, R. A.; Crossley, M. J.; Hush, N. S. *Inorg. Chem.* **1991**, *30*, 1259−1264.
(5) See ref 4 and references therein.
(6) Momenteau, M.; Loock, B.; Bisagni, E.; Rougee, M. *Can. J. Chem.* **1979**, *57*, 1804.

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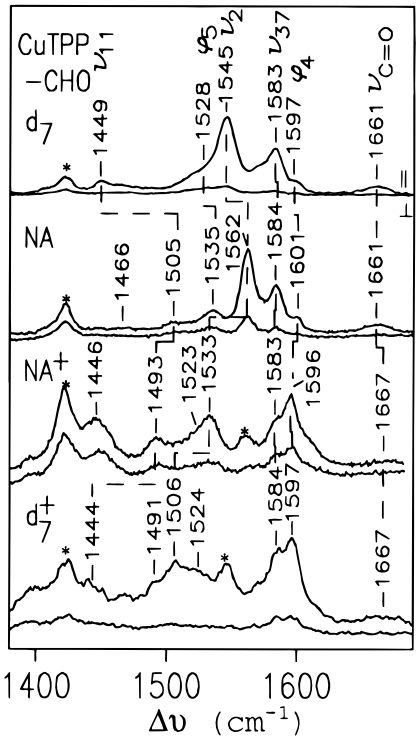

Figure 3. 457.9 nm excited RR spectra of CuTPP-CHO (NA), CuTPP-d_7-CHO and their cation radicals (NA^+, d_7^+) (1450−1700 cm^{-1}) in parallel (||) and perpendicular (⊥) polarizations. Cations were generated electrochemically, in CH_2Cl_2/0.1 M TBAP. Asterisks (*) mark solvent bands and residual neutral species bands.

Resonance Raman Spectroscopy. Soret band RR spectra (457 nm) were obtained with a Spectra Physics 2025 argon ion laser, and Q-band spectra (530 and 568 nm) were obtained with a Coherent Inova 100K-3 krypton ion laser. Spectra were collected in 135° backscattering geometry and dispersed through a Spex 1404 double monochromater to a cooled RCA 31034A photomultiplier tube or through a Spex triple monochromator with a cooled Princeton Instruments IRY-1024 diode array detector. Spectra were obtained at room temperature, except for those of the CuTPP-OCH_3^+ cation, which was obtained under an inert atmosphere at low temperature (∼−60 °C).[7] Q-band spectra of the neutral molecules were obtained in CH_2Cl_2 in a spinning NMR tube.

The porphyrin radical cations (approximately 1 mM porphyrin in CH_2Cl_2/0.1 M TBAP) were generated by in-situ spectroelectrochemistry in a bulk electrolysis cell similar to the one described by Czernuszewicz and Macor.[7] The electrolysis was controlled with a PAR 173 potentiostat and a PAR 175 controller. The progress of the oxidation was monitored by a change in sample color and by disappearance of the strong ν_2 RR band of the neutral molecules. Reversibility was established by reducing the cation to obtain the neutral species RR spectrum after completion of the experiment. CuTPP-NH_2^+ was unstable during the time required to obtain the RR data.

Results

RR spectra of the β-substituted molecules are similar to those of the parent CuTPP (Figure 2) but contain extra bands reflecting the lowering of molecular symmetry, from D_{4h} to C_s. The principal extra band in the Soret-excited (457 nm) spectra is at ∼1575 cm^{-1}, between the skeletal mode ν_2 and the phenyl mode ϕ_4. It is assigned to the skeletal mode ν_{37}, which is active only in the infrared spectrum for CuTPP,[3,8] but becomes activated in the RR spectra of CuTPP-β by the loss of the symmetry center. This assignment is based on the d_7 isotope shifts of CuTPP-CHO (Figure 3), which are similar to the d_8 isotope shifts in CuTPP.[8] The ν_{37} mode is principally $C_\alpha C_m$ stretching in character[9] and is little affected by β-deuteration, while ν_2 has significant $C_\beta C_\beta$ stretching character[9] and has an appreciable (17 cm^{-1}) d_7 shift. An alternative assignment, to the $C_\alpha C_m$

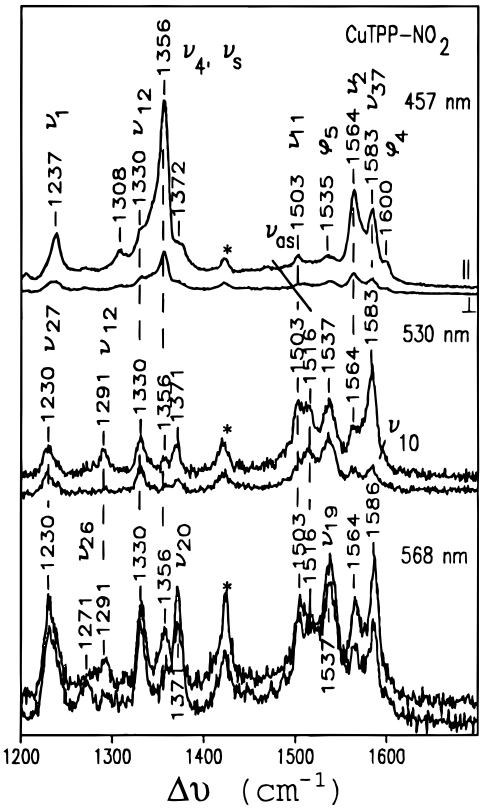

Figure 4. RR spectra of CuTPP-NO_2: (top) 457.9 nm excitation, in CH_2Cl_2, 0.1 M TBAP; (middle) 530 nm excitation in CH_2Cl_2; (bottom) 568 nm excitation in CH_2Cl_2. Parallel (||) and perpendicular (⊥) polarizations are shown. Asterisks (*) mark a solvent band.

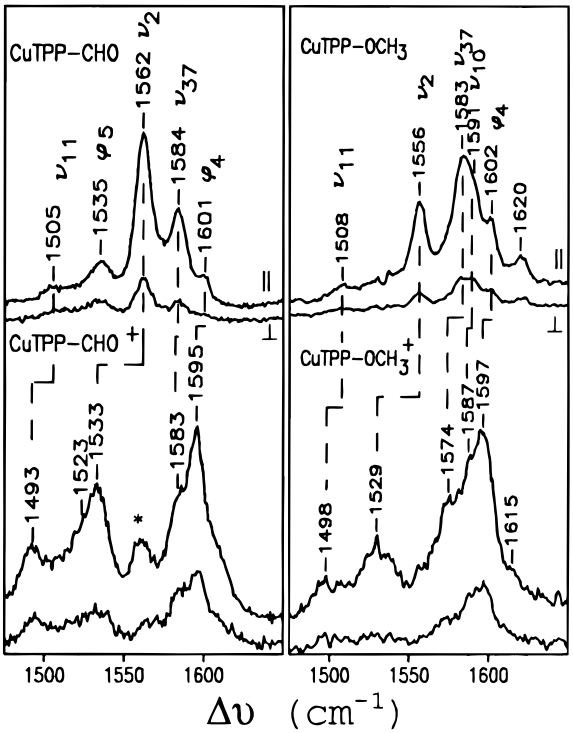

Figure 5. RR spectral comparison of CuTPP-CHO (left panel) and CuTPP-OCH_3 (right panel) and their cation radicals. Parallel (||) and perpendicular (⊥) polarizations are shown for each spectrum. Asterisks (*) mark residual neutral species bands.

(7) Czernuszewicz, R. S.; Macor, K. A. *J. Raman Spectrosc.* **1988**, *19*, 553.
(8) Hu, S.; Spiro, T. G. *J. Am. Chem. Soc.* **1993**, *115*, 12029−12034.

Table 1. Resonance Raman Frequencies of the CuTPP-β Neutrals and Their Cation Radicals[a]

mode[b]	CuTPP[c]	CuTPP$^+$	CuTPP-NO_2	CuCTPP-NO_2^+	CuTPP-CHO	CuTPP-CHO$^+$	CuTPP-CH_2OH	CuTPP-CH_2OH^+	CuTPP-Ac[d]	CuTPP-Ac$^+$	CuTPP-OCH_3	CuTPP-OCH_3^+ [e]
ϕ_4	1599	1595	1600	1595	1601	1597	1601	1597	1599	1597	1602	1597
ν_{37}	1582		1583	1584	1584	1583	1574	1569	1581	1569	1583	1574
ν_2	1562	1530	1564	1531	1562	1533	1554	1527	1554	1523	1556	1529
ν_{11}	1500	1496	1503		1505	1493	1509	1504	1503	1503	1508	1498
ν_4	1365	1355			1367	1364	1368	1360	1369	1366	1372	1360
ν_1	1237	1234	1237	1235	1237	1237	1238	1234	1237	1236	1235	1233
ν_9	1080	1181	1083	1079	1081	1082	1081	1079	1079	1076	1078	1077
ν_6	1008	1002	1006	1005	1004	1009	1006	1007	1006	1007	1006	1005
ν_7	886	884	890	896	887	893	891	887	888	885	888	886

[a] Resonance Raman data obtained in CH_2Cl_2/0.1 M TBAP solution with 457.9 nm excitation. [b] Mode designations according to Li et al.[9] [c] CuTPP = copper tetraphenylporphyrin. [d] Ac = $NHCOCH_3$. [e] Obtained at −60 °C.

mode ν_{10},[3,9] can be ruled out by the Q-band-excited spectrum (Figure 2), in which ν_{10} appears on the high-energy side of ν_{37} and is identifiable by its depolarized character. Sufficient memory of the D_{4h} parent symmetry is retained so that Q-band scattering mainly enhances depolarized bands, deriving from B_{1g} and B_{2g} modes (ν_{10}, ν_{11}, ν_{27}), and anomalously polarized bands, deriving from A_{2g} modes (ν_{19}, ν_{20}).

All CuTPP-β molecules give similar RR enhancement patterns, although additional bands associated with β-substituent modes can sometimes be detected. For example, the aldehyde C═O stretch can be seen at 1661 cm^{-1} for CuTPP-CHO (Figure 3), while for CuTPP-NO_2 (Figure 4), the symmetric and asymmetric NO_2 stretches, ν_s and ν_{as}, can be seen at 1356 and 1537 cm^{-1} (1349 and 1531 cm^{-1} in nitrobenzene).[10] Interestingly, ν_{as} is enhanced with Q-band excitation (530, 568 nm), while ν_s is enhanced with Soret excitation (457 nm), apparently by borrowing intensity from ν_4, which is ordinarily the strongest band in the Soret-excited spectrum (Figure 2).

CuTPP-CHO reveals characteristic changes in its Soret-excited RR spectrum upon oxidation to the radical cation, for which assignments were also confirmed by d_7 labeling: (1) The ϕ_4 and ϕ_5 phenyl bands become much stronger, relative to the skeletal bands. (2) The $C_\beta C_\beta$ stretching modes ν_2 and ν_{11} downshift strongly (29 and 12 cm^{-1}), while the $C_\alpha C_m$ stretching mode ν_{37} is unaffected. This behavior, also observed for CuTPP,[3,8] is exactly as expected for an a_{2u} radical.[3] The phenyl mode enhancement reflects increased involvement of the phenyl groups in the resonant electronic transition as a result of the concentration of the a_{2u} electron density on the C_m atoms (Figure 1), to which the phenyl groups are attached. At the same time, the $C_\beta C_\beta$ force constant weakens because of the $C_\beta C_\beta$ bonding character of the a_{2u} orbital, while the $C_\alpha C_m$ force constant remains unaltered, since very little of the a_{2u} electron is on the C_α atoms. Interestingly, the formyl C═O stretch upshifts slightly (6 cm^{-1}), implying a_{2u} antibonding character for the C═O bond. A similar effect is seen in radical cations of chlorophyll[11] and related compounds.[12]

When the CuTPP-OCH_3^+ radical was examined, it showed essentially the same RR pattern as CuTPP-CHO$^+$ (Figure 5). ϕ_4 again becomes stronger than the skeletal modes, while the

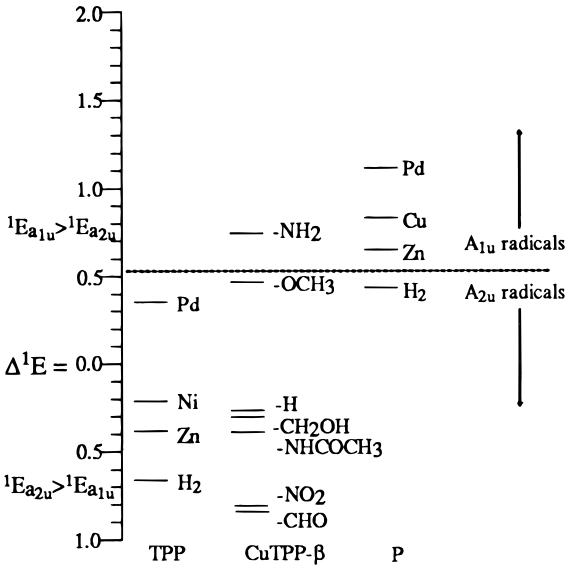

Figure 6. Absorption intensity-derived energy differences between the a_{1u} and a_{2u} orbitals in the indicated metalloporphyrins (P = porphine) according to Spellane et al.[14] The entries for CuTPP-β are from the present work. The dashed line represents the 0.326 eV offset between the neutral singlet state $\Delta E = 0$ and the cation radical $\Delta E = 0$ to account for exchange and Coulombic interactions.[14]

ν_2 and ν_{11} modes downshift strongly (27 and 10 cm^{-1}). In this case, ν_{37} downshifts as well (9 cm^{-1}), reflecting some mixing in of $C_\beta C_\beta$ character; the extent of this mixing is variable among different metalloporphyrins.[9] The observed parallelism between CuTPP-OCH_3^+ and CuTPP-CHO$^+$ is unexpected, since OCH_3 is strongly electron donating and is expected to have $a_{1u} > a_{2u}$ on the basis of the analysis by Binstead et al.[4] The a_{1u} orbital has nodes at the C_m atoms and is antibonding with respect to the $C_\beta C_\beta$ bonds. Thus the $C_\beta C_\beta$ modes, especially ν_2, are expected to increase in frequency, and modes of the C_β, rather than the C_m, substituents are expected to become prominent. This pattern is indeed seen experimentally for a_{1u} cations.[3,13] Other CuTPP-β donor substituents, $-CH_2OH$ and $-NHCOCH_3$, also give rise to the same RR enhancement and shift pattern upon radical cation formation (Table 1). There is no indication of a_{1u} radical formation in any of the species examined.

What is the source of this apparent discrepancy between the HOMO as identified by Binstead et al.[4] and that indicated by the radical cation RR spectra? We propose that orbital energy

(9) Li, X.-Y.; Czernuszewicz, R. S.; Kincaid, J. R.; Su, Y. O.; Spiro, T. G. *J. Phys. Chem.* **1990**, *94*, 31−46.
(10) (a) Varsanyi, G. *Vibrational Spectra of Benzene Derivatives*; Academic: New York, 1969. (b) Rao, C. N. R. In *The Chemistry of Nitro and Nitroso Compounds*; Feuer, H., Ed.; J. Wiley and Sons: New York, 1969. (c) Pinchas, S.; Samuel, D.; Silver, B. L. *Spectrochim. Acta* **1964**, *20*, 179.
(11) Lin, C.-Y.; McGlashen, M. L.; Hu, S.; Shim, Y. K.; Smith, K. M.; Spiro, T. G. *Inorg. Chim. Acta* **1996**, *252*, 179−184.
(12) (a) Babcock, G. T.; Callahan, P. M. *Biochemistry* **1983**, *22*, 2314−2319. (b) Lopez-Garriga, J. J.; Babcock, G. R.; Harrison, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 7241−7251. (c) Zwarich, R.; Smolarek, J.; Goodman, L. *J. Mol. Spectrosc.* **1971**, *38*, 336−357.
(13) (a) Sibilia, S. A.; Hu, S.; Piffat, C.; Melamed, D.; Spiro, T. G. *Inorg. Chem.* **1997**, *36*, 1013−1019. (b) Barzilay, C. M.; Sibilia, S. A.; Spiro, T. G.; Gross, Z. *Chem. Eur. J.* **1995**, *1*, 222−231. (c) Jayaraj, K.; Terner, J.; Gold, A.; Roberts, D. A.; Austin, R. N.; Mandon, D.; Weiss, R.; Bill, E.; Müther, M.; Trautwein, A. X. *Inorg. Chem.* **1996**, *35*, 1632−1640.

Table 2. Q_0/Q_1 Ratios for the CuTPP-β Porphyrins[a]

CuTPP-OCH_3	0.279	CuTPP-NO_2	0.647
CuTPP-CH_2OH	0.099	CuTPP-CHO	0.692
CuTPP-$NHCOCH_3$	0.174		

[a] Ratios obtained from the peak height at λ_{max} of the absorption spectrum in CH_2Cl_2.

changes associated with formation of the radical cation itself are responsible. Spellane et al.[14] have pointed out that the relative energies of a_{1u} and a_{2u} orbitals are expected to differ in neutrals and their radical cations because of differing exchange integrals. In Figure 6, we reproduce the orbital energy plot worked out for different metalloporphines and TPP's by Spellane et al., using the ratio of absorptivities for the $Q_{0,0}$ and $Q_{1,0}$ transitions:

$$A(Q_{0,0})/A(Q_{1,0}) = (\text{constant})({}^1E_{a_{2u}e_g} - {}^1E_{a_{1u}e_g})^2$$

Also included are values for the CuTPP-β species, based on their Q_0/Q_1 absorptivity ratios (Table 2). The order of CuTPP-β orbital energies is similar to that obtained by Binstead et al.,[4] although the $-NHCOCH_3$ and $-CH_2OH$ substituents are predicted to lie slightly below the a_{1u}/a_{2u} crossover, instead of slightly above it. Both $-OCH_3$ and $-NH_2$ are definitely above the crossover in both analyses, as far as the neutral molecules are concerned.

However, Spellane et al.[14] drew the line between a_{1u} and a_{2u} radicals at $\Delta^1E = 0.53$ eV, the expected crossover value for triplet excited states, on the expectation that the same crossover would be found for radical cations (assuming electron−hole interaction integrals and solvation energies cancel[14]). This division places all metalloporphine (as well as OEP) radicals in the a_{1u} category and all metallo-TPP radicals in the a_{2u} category, consistent with experiment.[3] It also leaves CuTPP-OCH_3^+ on the a_{2u} side of the line, consistent with the present RR data, although the orbital order is reversed in the neutral parent, consistent with the analysis by Binstead et al. CuTPP-NH_2^+ is predicted to be on the a_{1u} side of the divide, $-NH_2$ being an even stronger donor than $-OCH_3$. Unfortunately, the RR spectrum of CuTPP-NH_2^+ could not be obtained because of the oxidative instability of the $-NH_2$ group.

Thus we conclude that the RR data are consistent with the orbital ordering among the CuTPP-β derivatives, on the basis either of electrochemical and optical energies[4] or of the absorptivities,[14] provided account is taken of the expected a_{2u} orbital energy elevation in radical cations, relative to neutrals, because of the differing exchange interactions.

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(14) Spellane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. *Inorg. Chem.* **1980**, *19*, 386−391.