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Invited talk at the "First Conference on the Progress in X-ray Studies by Synchrotron Radiation", Strasbourg, April 1-4, 1985.

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POLARIZED X-RAY ABSORPTION NEAR EDGE STRUCTURE OF HIGHLY OXIDIZED Cr PORPHYRINS(*)

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ABSTRACT

Polarized X-ray absorption near edge spectra have been measured for Cr(IV)(TTP)O and Cr(V)(TTP)N (TTP is the dianion of 5, 10, 15, 20-tetra-p-tolylporphyrin). These spectra, which are very similar for the two molecules, show an intense pre-edge absorption feature polarized perpendicular to the porphyrin plane. The absorption edges are relatively featureless when the polarization is parallel to the porphyrin plane. On the basis of multiple-scattered-wave X calculations the intense pre-edge feature is interpreted as a bound-- bound transition with significant metal character in the excited state. This transition, which has been observed in many metal-oxo species, was not observed in the putative ferryl (Fe=O) intermediates of horseradish peroxidase. The reasons for this absence in Fe=O species, and its relationship to the reactivity of metal-oxo porphyrin complexes, are discussed in light of the present results.

(*) Invited talk at the First Conference on the Progress in X-ray Studies by Synchrotron Radiation, April 1-4, 1985, Strasbourg (France).

When a core electron is excited with a sufficiently energetic photon, transitions to high-lying bound states and to the continuum are possible. For transition metals, X--ray photons have the appropriate energy to excite a 1s electron. The resulting X-ray absorption spectra are characterized by an abrupt increase in absorbance (an absorption edge) at the excitation threshold. The absorption is frequently highly structured, both in the edge region and for ~1000 eV above the edge. For the extended X-ray absorption fine structure (EXAFS) region, >50 eV above the edge, single scattering treatments give an adequate desciption of most the structure[1]. In contrast, theoretical interpretation of edge spectra has proven difficult since in this region the long wavelength of the excited photoelectron permits extensive multiple scattering interactions. Despite the theoretical difficulties, there is great interest X-ray edge spectra since they are quite sensitive to the detailed molecular geometry around the absorbing atom.

Recently, polarized spectra have been used to simplify the interpretation of X-ray absorption edges[2]. Such measurements are possible as a result of the nearly 100% linearly polarized character of synchrotron radiation. For K absorption edges, the initial state is the totally symmetric 1s orbital, hence the polarization properties of the edge structure are a direct reflection of the symmetry properties of the final state. This symmetry information provides additional information against which calculated edge spectra can be compared. In recent work the combination of polarized measurements and multiple-scattered-wave $X\alpha$ calculations has proven to be a useful tool for interpreting the X-ray absorption edge structure of Mo[3] and Cu[4] complexes. We report here the results of applying these experimental and theoretical approaches to the X-ray absorption edge spectra of selected highly oxidized metalloporphyrin complexes.

Metalloporphyrins are found at the active site of many metalloproteins. For the heme mono-oxygenase and peroxidase enzymes, a highly oxidized iron porphyrin is thought to be present at the active site. A particularly well studied example of this type of enzyme is the peroxidase isolated from horseradish roots. The catalytic cycle (Scheme I) of horseradish peroxidase (HRP) involves initial oxidation to the formally Fe(V) compound I (HRP-I). On reaction with substrate, HRP-I is reduced to the formally Fe(IV) compound II (HRP-II) which in turn reacts with substrate to regenerate resting HRP. Both HRP-I and HRP-II are thought to contain an Fe(IV) ferryl potphyrin, (por)Fe=O, with the extra oxidation equivalent in HRP-I residing in a porphyrin π-cation.

Ferryl porphyrins have limited stability, however analogous metal-oxo complexes of the earlier transitions metlas (Ti, V, Cr) are quite stable and have been studied extensively. A characteristic feature of the X-ray absorption edge spectra of metal-oxo complexes is the presence of a very intense pre-edge transition[5]. Recently, X-ray absorp-

tion spectra have been measured for HRP-I and HRP-II, and for closely related model compounds[6]. The EXAFS data for these species showed the expected short (~1.6 Å) Fe-O bond, however the absorption edges lacked the characteristic intense metal-oxo pre-edge transition.

In order to elucidate the general features of (porphyrin) M=O absorption edge structure, we have measured polarized X-ray absorption edge spectra for (TTP)Cr(IV) = O(1). In contrast with the ferryl species, chromyl porphyrins are sufficiently stable to be crystallized. For comparison, we have also examined the polarized absorption edge spectra of (TTP)Cr(V) ≡ N(2). The polarized X-ray absorption edge structure for these complexes, and for a ferryl porphyrin, were calculated using a multiple-scattered-wave Xα approach.

EXPERIMENTAL

X-ray absorption measurements. X-ray absorption data were measured as fluorescent excitation spectra, using an array of 17 NaI(Tl) detectors. Data were collected at the Stanford Synchrotron Radiation Laboratory under dedicated conditions (3.0 GeV, ~50 mA) on the focused beam line II-2. A v-slit was used to decrease the horizontal acceptance of the mirror to 1 mrad in order to improve the energy resolution. Energy monochromation was achieved using a Si(220) double crystal monochromator. The absorption spectrum of a Cr foil was measured simultaneously with measurement of the Cr (porphyrin) data and relative energies were calibrated with respect to the first inflection point of the Cr metal absorption edge, defined to be 5988.8 eV. The fluorescence data for each detector channel were examined visually for the presence of Bragg diffraction peaks. After removing the Bragg peaks, using a linear interpolation, a weighted average[7] of the different channels was calculated for each scan. The data shown represent the average of 3-4 scans of ca. 15 min each. The total irradiation time, including EXAFS measurements (to be reported elsewhere) was ca. 12 hours for each crystal. Comparison of diffraction intensities before and after the absorption measurements showed no evidence of radiation induced crystal decomposition.

Crystal orientation and alignment. Crystals of the Cr porphyrins were prepared as previously described[8,9]. Crystals of 1 and 2 are isomorphous, with space group $P2_1/c$ and 4 molecules per unit cell. The structure is such that the two distinct Cr=O (or Cr≡N) directions differ by 3°. Individual crystals were mounted in a sealed capillary to prevent evaporation of mother liquor. The crystals selected for studied had dimensions 0.9x x0.3x0.2 for 1 and 1.2x0.4x0.4 for 2. Crystal orientations were determined using a Syntex

$P2_1$ automated diffractometer and the crystals were oriented and aligned in the X-ray beam as previously described[2,4]. The three orientations which were examined for each crystal are defined in Fig. 1.

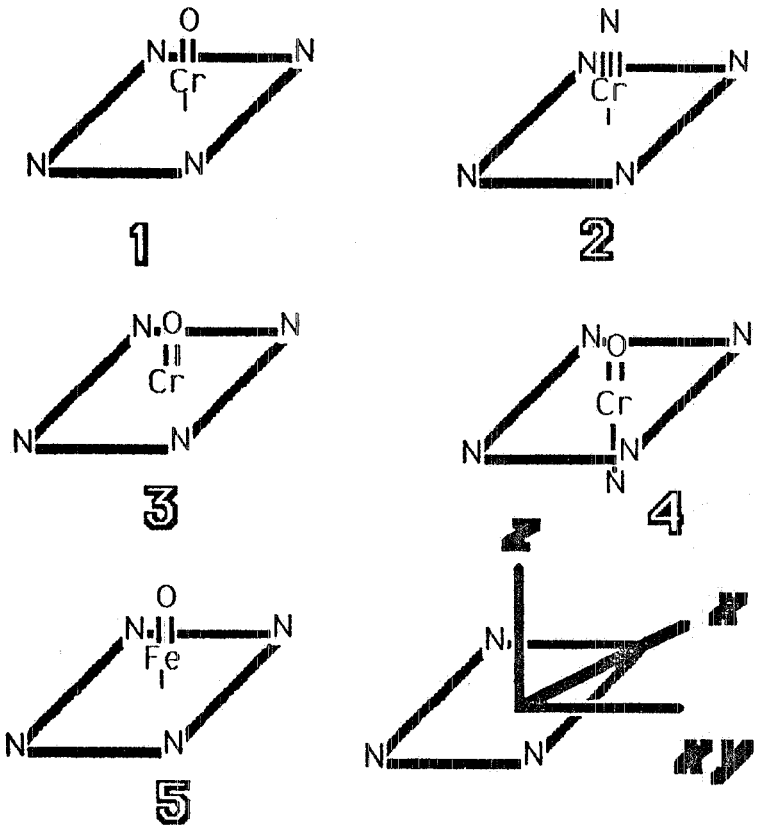

Fig. 1 - Molecules studied. The porphyrin moiety is abbreviated as a parallelogram containing four nitrogens. The axial imidazole is shown as a single N. Molecules 1 and 2 exist and were studied experimentally; all 5 species were studied theoretically. The three experimental orientations of the polarization vector relative to the porphyrin are shown by the arrows labeled x, xy and z.

Theoretical calculations. Theoretical calculations were performed in a multiple-scattered wave Xα (MSW Xα) framework[10], using the "extended continuum" method[11]. In this approach, final states with energies greater than V_{II} (the interstitial potential) are treated with continuum-like boundary conditions. An outer sphere is not used and the interstitial region is extended to infinity. This method is useful not only for energies greater than zero (true continuum region) but also for $V_{II} < E < 0$. This latter region corresponds to bound final-states in self-consistent calculations. Extended continuum and self-consistent calculations give similar results, however the former requires considerably less computation. In all calculations, the angular basis functions we

re truncated at l=5 for all atomic centers and extended to l=10 for the outer region. Lifetime and instrumental broadening effects were accounted for by convolving the calculated spectra with a Lorentzian function of width 2 eV.

Spectra were calculated using several different muffin tin radii. Variations in muffin tin radii gave significant changes in the relative amplitudes of different transitions, but no change in the calculated energies. Thus, while relative energies are meaningful, the agreement between calculated and experimental amplitudes may be regarded as somewhat fortuitous. In the past, 15% overlap of muffin tin radii has been found to give good agreement between theoretical and calculated spectra. This overlap was used for all of the spectra shown here.

Polarized edge spectra were calculated for the known, five-coordinate, complexes 1 and 2 and for several related hypothetical complexes (see Fig. 1). The latter included five-coordinate complexes with the Cr in the plane (3 and 4), a six coordinate of chromyl TTP (5) and a five-coordinate ferryl analog (6). In all cases, the complexes studied were idealized to C_{4v} symmetry. The porphyrin ring was approximated by four equatorial nitrogens and the axial imidazole in 6 by a single nitrogen, thus giving 6 or 7 atom clusters. Bond lengths and angles were taken from the known structures of 1 and 2 with the exception of the axial Cr-N bond in 5, which was taken as 2.0 A. Spectra were calculated for $\hat{e}||z$ and $\hat{e}||x$ (see Fig. 1). The idealized C_{4v} symmetry requires that the calculated x and xy orientation be identical.

RESULTS

The polarized X-ray absorption edge spectra of 1 and 2 in the x and z orientations are shown in Fig. 2. The most striking feature of these spectra is the intense pre-edge

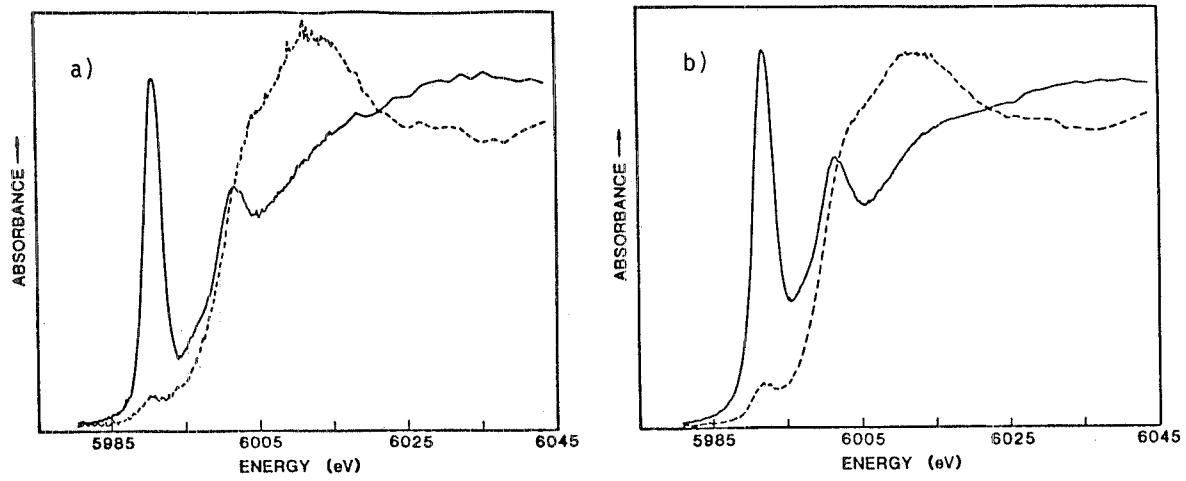

Fig. 2 - Polarized X-ray absorption edge spectra for chromium porphyrins. Solid curve is $\hat{e}||z$, dashed curve is $\hat{e}||x$ (see Fig.1 for definitions). a) Cr(IV)=O(TTP); b) Cr(V)≡≡N(TTP). Note the ~1 eV shift in the energy of the white line between Cr(IV) and Cr(V). All spectra have been normalized to give an edge jump of 1.0.

absorption feature at ~5990 eV. This feature is nearly completely z polarized. The small intensity of this transition observed for the x orientation can be accounted for by the imperfect alignment of symmetry related molecules in the unit cell and by the incomplete polarization of the X-ray beam. The energy of this transition varies by 1 eV between 1 (5991 eV) and 2 (5992 eV).

The xy orientation (not shown) is nearly identical to the x orientation, except in the vicinity of 6005 eV. The difference between x and xy arises from the less than 4-fold symmetry of the porphyrin. For both 1 and 2, the porphyrin is strongly buckled (saddle-shaped)[8,9].

The calculated edge spectra for 1 and 2 are compared in Fig. 3. The plot limits have been chosen to correspond approximately to those used in Fig. 2. In qualitative terms,

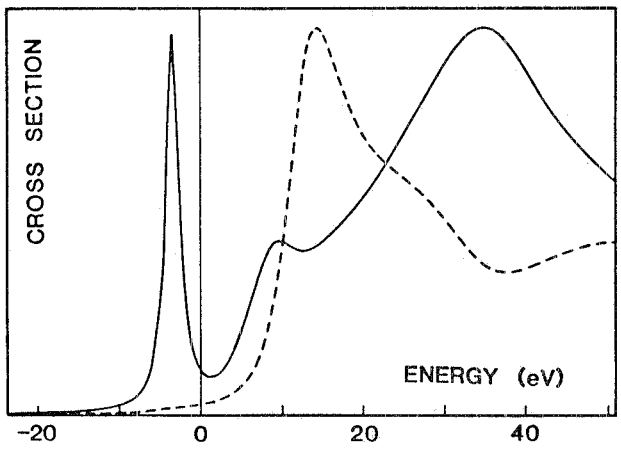

Fig. 3 - Calculated X-ray absorption edge spectra for chromium porphyrins. Calculated spectra corresponding to experimental spectra shown in Fig.2. The fermi level is shown by the vertical line. Energy scale has been chosen to facilitate comparison with experimental spectra.

the calculated spectra are strikingly similar to the experimental spectra, although) (vide supra) this agreement is sensitive to the size of the muffin tin radii. The final state for this transition is composed of approximately 57% Cr-d and 13% O-p orbitals.

In order to test the sensitivity of the calculations to the details of the geometry, we calculated spectra for the hypothetical molecules 3-5 (Fig. 4). In the context of

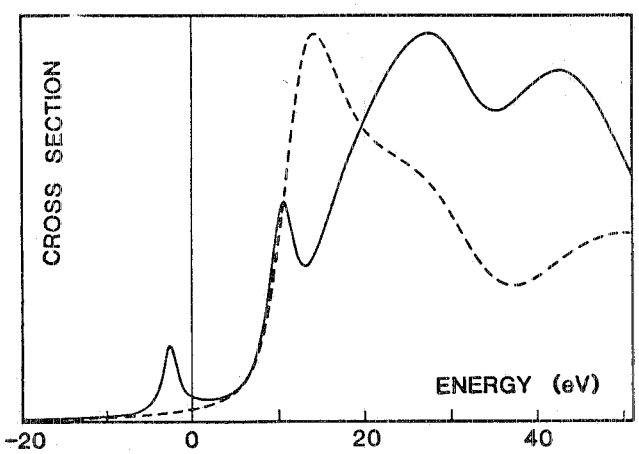

Fig. 4 - Calculated X-ray absorption edge spectra for a hypothetical 6-coordinate chromium porphyrin. Spectra for the hypothetical molecule 4. Solid curve is $\hat{e} \| z$, dashed curve is $\hat{e} \| x$ (see Fig.1 for definitions). Note the appearance of a new transition in the z direction.

our simplified model, the displacement of the Cr from the plane had no effect on the calculated spectra. Inclusion of an axial nitrogen had no effect on the $\hat{e} \| x$ spectrum, but resulted in a new, broad resonance lying ~30 eV above the pre-edge spike, in the $\hat{e} \| z$ spectrum. This feature occurs at the same energy as a shoulder on the high energy side of the principal maximum in the x polarized spectrum.

In contrast with the relative insensitivity to molecular geometry, the calculated spectra are quite sensitive to the identity of the metal atom. The calculated spectra for the hypothetical five-coordinate ferryl complex 5 are shown in Fig. 5. The most striking feature of these spectra is the absence of the intense pre-edge transition in the z-polarized spectrum. Except for this change, the calculated spectra for 5 is very similar to the isostructural complex 1.

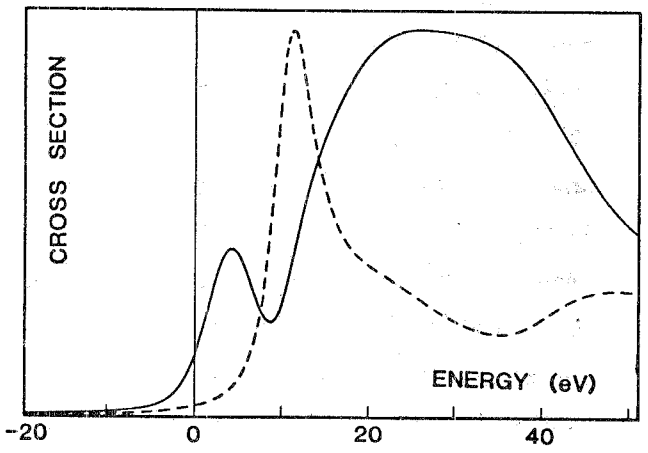

Fig. 5 - Calculated X-ray absorption edge spectra for a 5-coordinate ferryl porphyrin. Spectra for 5. Scale and plotting format same as Figs.2-4. Note the absence of pre-edge spike in z orientation. Calculations do not include quadrupole transitions, hence the weak, quadrupole coupled 1s→3d transition is absent.

DISCUSSION

Intense pre-edge transitions are common in first-row transition metal M=O complexes. In the case of CrO_4^{2-}, MSW X calculations indicated that this feature was due to a transition to a bound state of primarily metal d character[12]. Polarized measurements of the V=O[13] and the O=U=O[14] units indicated that the metal-oxo pre-edge peak is strongly polarized in the direction of the M=O bond. On the basis of these results, it was suggested that the bound-state responsible for the pre-edge transition is a molecular orbital containing metal d and oxigen p_z. Our results, consistent with these previous measurements, show that the pre-edge feature in 1 and 2 is strongly z polarized. The apparent presence of a small pre-edge feature in the x and xy polarized spectra can be accounted for by the crystal structure, which gives a slight misalignment of the two different M=O directions, and by the incomplete polarization of the beam.

The pre-edge feature is ca. 100 times more intense than the dipole forbidden 1s--3d transition in centrosymmetric complexes. This intensity is only consistent with a dipole--allowed, p-symmetry final state. The pre-edge transition has a well defined energy, with a fwhm of 2.8 eV for 1 and 3.5 eV for 2. This width is comparable to the lifetime and monochromator broadening, and is indicative of a bound final state. In contrast, non-bound continuum features are generally very broad (fwhm ~10-20 eV)[4].

In general, metal-localized bound-- bound transitions are expected to be reasonably insensitive to the details of the molecular geometry, while continuum shape-resonance features are expected to have a strong geometric dependence. Our calculations show that the pre-edge feature is insensitive to molecular geometry, with essentially no change between the 5 and 6 coordinate models, consistent with bound final-state character for this transition. In contrast, all of the higher energy features, and in particular the new z-polarized feature in the 6-coordinate calculation, show behavior expected for continuum resonances.

The energy of continuum resonance features is approximately proportional to $1/R^2$, where R is the absorber-scatterer distance[15]. The only difference between the calculated spectra for 1 and 4 is the presence of a new z polarized peak in 5. This new peak occurs at the same energy as a shoulder observed in the calculated x polarized spectra (at ~ 25 eV). Both features are reasonably assigned as continuum resonances involving the axial (or pyrrole) nitrogen. In both cases the Cr-N distance was 2 Å, hence the continuum resonances are expected to occur at the same energy. In addition, it is interesting to note that the x and xy (not shown) polarized experimental spectra only differ at ~6005 eV. Given the Cr-N (pyrrole) continuum resonance assignment at 6015 eV, a feature at 6005 eV would correspond to an atom at 3-4 Å. This is completely reasonable, since it is only for the more distant carbon atoms that the deviations of the porphyrin from C_{4v} symmetry become significant.

The pre-edge transition for 2 is shifted by 1 eV to higher energy relative to 1. This is consistent with the increase in formal oxidation state from Cr(IV) to Cr(V). There is no discernable shift in the energies of the higher energy features between Cr(IV) and Cr(V). This is not surprising since the Cr oxidation state is expected to have relatively little effect on the relative energies of the initial 1s state and continuum final states while oxidation state will have a large effect on the energy of the 3d state.

In a molecular orbital picture, the vacant orbital involved in the pre-edge transition can be viewed as an antibonding combination of metal d and ligand p orbitals. For d^2 Cr(IV), this antibonding orbital is the highest lying unoccupied orbital, and is

thus completely filled on the addition of two electrons (e.g., for d^4 Fe(IV)). This picture, while overly simplistic, serves to illustrate the ability of polarized X-ray absorption edge spectroscopy to probe the energy and symmetry of unoccupied molecular orbitals. In this view, X-ray absorption edge spectra, by probing vacant orbitals, are complementary to X-ray photoelectron spectra, which probe filled orbitals.

Buchler has noted that relative reactivities are TiO(Por) ~ VO(Por) << CrO(Por) < < MnO(Por) < FeO(Por), and this was attributed to the increased number of d electrons causing an increased repulsion of the p electron pairs at the terminal oxo group, thus destabilizing and activating oxygen atom[16]. This is consistent with our results where we see the Fe=O system having a filled anti-bonding orbital and hence being the most reactive. Also consistent with why analogous species do not exist for later transition metals, since adding still more electrons would prevent formation of M=O to begin with. This would account for, for example, the suprising thermal stability of Mn(V)N porphyrins[17], since they are (formally) isoelectronic with Cr(IV).

Axially polarized intense pre-edge transitions have also been observed for square-planar Cu complexes[4]. Despite their outward similarity, the copper transition appear to arise from a different mechanism. The copper pre-edge transition occurs close in energy to the principal absorption maximum and the intensity of the pre-edge feature decreases as the axial bond length decreases. Although models are not available to test the dependence of the Cr pre-edge transition on a sixth axial ligand, the calculations suggest that the pre-edge spike is independent of the presence or absence of a ligand trans to the M=O. These features are consistent with the 1s-- 3d assignment for Cr=O and the 1s--- 4p assignment for square-planar Cu.

CONCLUSIONS

Polarized X-ray absorption edge measurements of chromium oxene and nitrene porphyrins have revealed the presence of an intense pre-edge transition polarized in the direction of the Cr=O or Cr≡N bond. Excellent agreement is found between the experimental spectra and spectra calculated using extended continuum, MSW Xα methods. The intense pre-edge transition is found to have predominantly metal d character, with a small amount of oxygen (or nitrogen) p character. The final state for this transition can be identified, in a molecular orbital picture, with a metal + ligand anti-bonding orbital. This identification provides a rationalization of the reactivity patterns of first-row metal-oxo porphyrins.

On the basis of the calculations, the pre-edge feature appears to be insensitive

to the molecular environment, as expected for a bound-- bound transition. In contrast, the broad transitions at ~6015 eV seem to behave like continuum resonances, with energies that are insensitive to oxidation state but increase for shorter metal-ligand bonds. For "normal" (e.g. non oxo) porphyrins, these continuum resonance will dominate the isotropic absorption spectra. This interpretation would suggest, therefore, that the energy of "normal" metalloporphyrin edges will depend primarily on the average metal-ligand bond length and only slightly on the metal oxidation state. This preciese effect has been observed for Fe porphyrins, where the edge energy varies with spin state changes but not with oxidation state changes[18].

Perhaps the most striking aspect of this work is the degree to which the experimental spectra are reproduced using a simple six atom model and non-self-consistent calculations. The relative ease of these calculations suggests that it may be feasible to use the MSW $X\alpha$ method to study low symmetry complexes, since it appears unnecessary to include more that the nearest neighbors to the metal. This finding is in conflict with previous theoretical studies which suggested that 30-50 atom clusters were required to obtain reasonable agreement with experiment[19].

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